On the Specificity of Aneurinase

By Kiku MURATA

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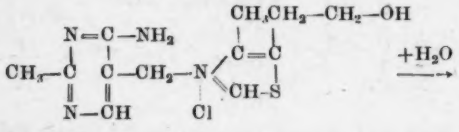
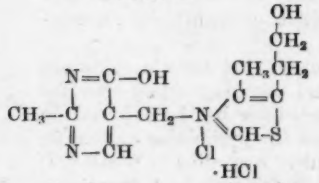
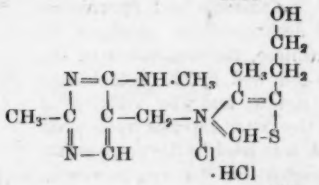
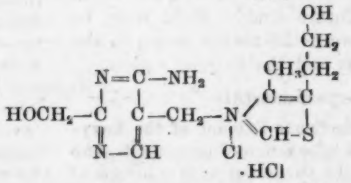
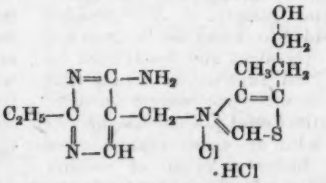
Aneurinase, which decmposes aneurin, has been found in shell-fishes by Fujita[1] and in fishes by Sealock.[2] The mode of the enzymatic decomposition has been studied by Fujita,[3][4][5] Yamasaki[6] and also by Woolley.[7] According to their results aneurin is splitted into pyrimidine and thiazole as follows;



To study the more precise mechanism of the action of aneurinase against aneurin, it is desirable to have some knowledge on the specificity of the enzyme in relation to the chemical constitution of the substrate. The author has, therefore, studied on the action of aneurinase on various aneurin analogues as described below, and the results are summarised in Table 1.

Table 1

Expt. No.	Substrate: Name	Substrate: Structure	Decomposition by Enz.
1, 2	4-methyl-5-β-hydroxyethyl-N-[(2′-methyl-4′-hydroxy-pyrimidyl-5′)-methyl]-thiazolium-chloride-hydrochloride (I)		−
3	4-methyl-5-β-hydroxyethyl-N-[(2′-methyl-4′-aminomethyl-pyrimidyl-5′)-methyl]-thiazolium-chloride-hydrochloride (II)		−
4, 5, 6	4-methyl-5-β-hydroxyethyl-N-[(2′-hydroxmethyl-4′-amino-pyrimidyl-5′)-methyl]-thiazolium-chloride-hydrochloride (III)		+
7, 8	4-methyl-5-β-hydroxyethyl-N-[(2′-ethyl-4′-amino-pyrimidyl-5′)-methyl]-thiazolium-chloride-hydrochloride (IV)		+

(1) Fujita and Numata, *J. Biochem. Soc. Japan*, **17**, 156 (1943); **18**, 63 (1944).
(2) Sealock, *J. Am. Chem. Soc.*, **65**, 935 (1943).
(3) Fujita and Numata, *J. Biochem. Soc. Japan*, **18**, 327 (1944).
(4) Fujita, Description of the 14 th meeting on special committee of V. B_1, (1947).
(5) Fujita and Hasegawa, Description of the 29th meeting on special committee of V. B_1, (1948).
(6) Yamasaki, *J. Jap. Soc. Food and Nutr.*, **1**, 8 (1948).
(7) Woolley, unpublished (it is introduced on *Ann. Review of Biochem.* (1944)).

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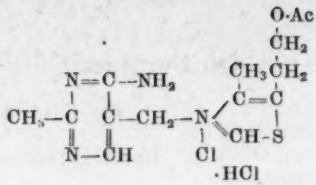
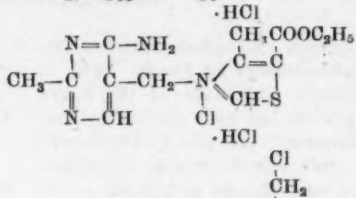
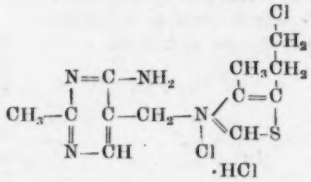
9 4-methyl-5-β-hydroxyethyl-N-[(2'-methyl-4'-amino-pyrimidyl-5')-methyl]-thiazolium-chloride-hydrochloride-acetate (V) +



10 4-methyl-5-carboethoxy-N-[(2'-methyl-4'-amino-pyrimidyl-5')-methyl]-thiazolium-chloride-hydrochloride (VI) +



11 4-methyl-5-β-chloroethyl-N-[(2'-methyl-4'-amino-pyrimidyl-5')-methyl]-thiazolium-chloride-hydrochloride (VII) +



From Table 1 it is clear that the side chain of the thiazole nucleus and some substitution at position 2 on the pyrimidine nucleus have no effect but the amino group at position 4 of the latter is absolutely necessary* for the hydrolytic decomposition of aneurin by aneurinase.

It may be presumed that aneurin splits into the pyrimidine and thiazole residues after the protein part of aneurinase has been joined to the amino group on the pyrimidine nucleus in the aneurin molecule. According to Woolley,[7] in the isolation of the thiazole and pyrimidine residues from the decomposition products by the action of aneurinase, the separation of the thiazole residue is followed by the detachment of the pyrimidine residue and the velocity of the detachment of the latter depends upon what species of shell-fish was used in the preparation of the enzyme. Reasons for this are, however, to be left in the future study; there may be some relation between the amino group in the pyrimidine nucleus and the enzyme action.

Experimental

Preparation of the Crude Extract of the Enzyme.—The meat and juice removed from shells were weighed together and triturated with addition of the sand. An equal quanity of $N/10$ sodium bisphosphate was added to it and the mixture was kept on standing over-night and centrifuged for 10 minutes. The clear supernatant liquid thus obtained was used as the crude enzyme extract.

Test for Enzymatic Activity.—The enzyme extract was mixed with an equal volume or a slightly excess of buffer solution of sodium acetate (pH 6.1) and a unit quantity of aneurin was added as shown in Table 2. After one hour at 60°, the reaction mixture was filtered and the content of aneurin remained in the filtrate was determined by the method of diazo or thiochrome. It was then possible to calculate the amount of aneurin decomposed by the ferment by subtracting the amount of aneurin remaining in the filtrate from what has been added originally.

Table 2

Reaction condition	Volume of enzyme extract, cc.	Substrate (V. B_1 analogues added), γ/cc.	Volume of buffer solution, cc.	Volume of $2N$ hydrochloric acid, cc.
1	6	200 γ/2 cc.	11.5	0.5
2	3	100 γ/1 cc.	6.0	——
3	10	150 γ/1.5 cc.	18.0	0.5
4	2	10 γ/1 cc.	2.0	——
5	24	120 γ/1.2 cc.	22.8	——
6	22	110 γ/1.1 cc.	20.9	——
7	20	300 γ/3 cc.	36.5	0.5
8	2	10 γ/1 cc.	17.0	——

The Main and Blank Tests.—Equal volumes of the enzyme extract were put in two round bottom flasks of about 100 cc. in volume, which are attached to reflux condensers through a ground glass joint. The one, to be used as a blank test, was boiled gently over the asbestos pad for three minutes to inactivate the enzyme. The rest of the operations was the same for the both tests. A unit quantity of the buffer and a substrate under consideration were added to each and warmed to 60° for one hour. At the end of the reaction, water droplets condensed at the neck of the flasks and the lower part of the condensers were mixed well with the reaction mixtures in order to keep the concentration constant. They were then filtered and the filtrates were subjected separately for the aneurin determination.

The determination of aneurin was made by the usual methods, the diazo and thiochrome, except in the cases of substrate (VI) and (VII), where the determinations were done in the alkaline solution because the thiochrome of these compounds were difficult to dissolve in isobutanol.

Since the value obtained by the main test indicates percentage of aneurin recovered, it is then

* Those compounds which do not possess the free amino group and undergo splitting with difficulty can be made to decompse with addition of an equal amount of V. B_1.

Table 3

Expt. No.	Reaction condition	Test	Substrate	Aneurin content, γ/cc.	Diazo method: Enzyme extract, cc.	Substrete (calculated) aneurin, γ	Aneurin recovered, γ	Recovery, %	Decomposition, %	Thiochrome method: Enzyme extract, cc.	Substrete (calculated) aneurin, γ	Aneurin recovered, γ	Recovery, %	Decomposition, %
1	1	Enz. act.	—	10	5	50	14.9	—	70.4	—	—	—	—	—
		Main	(I)	〃	〃	〃	41.5	—	3.1					
		Blank		〃	〃	〃	42.8	85.6	—			T. R. negative		
	2	Main		〃	〃	〃	33.2	—	0.3					
		Blank		〃	〃	〃	33.3	66.6	—					
2	3	Enz. act.	—	5	10	50	13.3	—	70.3	0.4	2·0	0.04	—	98.0
		Main	(I)	〃	〃	〃	41.6	—	4.2			T. R. negatiue		
		Blank		〃	〃	〃	43.4	86.8	—					
3	3	Enz. act.	—	5	10	50	6.8	—	86.4	—	—	—	—	—
		Main	(II)	〃	〃	〃	32.7	—	0			T. R. negative		
		Blank		〃	〃	〃	32.7	65.4	—					
4	3	Enz. act.	—	5	—	—	—	—	—	0.4	2.0	0	—	100.0
		Main	(III)	〃	10	50	2.3	—	95.2	—	—	—	—	—
		Blank		〃	〃	〃	47.6	95.2	—	—	—	—	—	—
5	4	Enz. act.	—	2	—	—	—	—	—	0.25	0.5	0.01	—	98.0
	5	Main	(III)	2.5	20	50	5.0	—	84.4	0.4	1.0	0.16	—	69.3
		Blank		〃	〃	〃	32.1	64.2	—	0.2	0.5	0.52	104.0	—
6	4	Enz. act.	—	2	—	—	—	—	—	0.25	0.5	0	—	100.0
	5	Main	(III)	2.5	20	50	0	—	100.0	0.4	1.0	0	—	100.0
		Blank		〃	〃	〃	48.1	96.2	—	0.2	0.5	0.53	106.0	—
7	4	Enz. act.	—	2	—	—	—	—	—	0.25	0.5	0	—	100.0
	6	Main	(IV)	2.5	18	45	0	—	100.0	0.4	1.0	0	—	100.0
		Blank		〃	〃	〃	46.7	104.0	—	0.2	0.5	0.49	98.0	—
8	4	Enz. act.	—	2	—	—	—	—	—	0.25	0.5	0	—	100.0
	7	Main	(IV)	5	10	50	10.0	—	81.7	0.2	1.0	0.18	—	64.0
		Blank		〃	〃	〃	54.4	108.0	—	0.1	0.5	0.50	100.0	—
9	4	Enz. act.	—	2	—	—	—	—	—	0.2	0.4	0	—	100.0
	5	Main	(V)	2.5	20	50	0	—	100.0	0.4	1.0	0	—	100.0
		Blank		〃	〃	〃	40.0	80.0	—	0.2	0.5	0.52	104.0	—
10	8	Enz. act.	—	0.5	—	—	—	—	—	2.0	1.0	0	—	100.0
		Main	(VI)	〃			D. R. negative			2.0	1.0	0	—	100.0
		Blank		〃						1.0	0.5	0·52	104.0	—
11	8	Enz. act.	—	0.5	—	—	—	—	—	2.0	1.0	0	—	100.0
		Main	(VII)	〃			D. R. negative			2.0	1.0	0.01	—	99.0
		Blank		〃						1.0	0.5	0.60	120.0	—
		Main		〃						2.0	1.0	—	—	100.0
		Blank		〃						1.0	0.5	0.48	96.0	—

possible to calculate its decompsition percentage. The blank test shows percentage of recovery of aneurin added originally; this value was compared with that obtained by the main test. These results are shown in detail in Table 3.

Conclusion

The experimental results show that the free amino group in the pyrimidine ring of aneurin molecule is essential for the decomposition of aneurin by aneurinase, but other groups in the pyrimidine or the thiazole nuclei have little influence on this hydrolytic decomposition.

The author wishes to express his sincere thanks to Dr. Matsukawa of Takeda Institute, who kindly furnished him with the aneurin analogues used in these experiments. Thanks are also due to Prof. Akabori at Osaka University for his painstaking revision of the paper and to Dr. Chachin, Director of this research institute, for his support in executing this work.

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Synthetic Mica Research*

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Introduction

Research in the production of synthetic mica was initiated in 1938 in response to the need of a local supply of high-grade mica. Experimental work was begun in January 1939 and directed originally to find compositions which crystallized easily. It was necessary to determine the temperatures of crystallization of mica in order to proceed with the work. The temperatures and velocities of crystallization were measured. Experiments to obtain large crystals were continued simultaneously with the above measurements. The corrosion of crucibles by the melt became more serious as the charge of melting increased and the rate of cooling decreased. Suitable crucibles for the synthetic work were investigated.

Temperatures of Crystallization and the Velocities of Crystallization of Synthetic Mica

The theoretical chemical formula of the fluorphlogopite is $KMg_3AlSi_3O_{10}F_2$ or 0.5 K_2O, 2.0 MgO, 1.0 MgF_2, 0.5 Al_2O_3, 3.0 SiO_2. If the ratio of MgO to MgF_2 in the folmula is varied, subsequent compositions can be represented by points in the three component system of phlogopite-orthoclase-magnesium fluoride.(1) By replacing the orthoclase with other silicates and the magnesium fluoride with other fluorides, various compositions are represented by points in three component systems.

Systems used in representing the various compositions are:

POM	phlogopite-orthoclase-magnesium fluoride(2)
P(K6S)M	phlogopite-(0.5K_2O, 3SiO_2)-magnesium fluoride 3)
P(KS)M	phlogopite-(K_2O, SiO_2)-magnesium fluoride 3)
POA	phlogopite-orthoclase-aluminium-fluoride(4)
PO(Ks)	phlogopite-orthoclase-potassium silicofluoride(4)

Table 1

Exptl. designation	Chemical composition, mol					Constitution			Temp. of crystn. °C.
	K_2O	MgO	Al_2O_3	SiO_2	MgF_2	Phlogopite	Orthoclase	MgF_2	
POM 1	0.50	2.00	0.50	3.00	1.00	1.0	——	——	1361
POM 2	0.51	1.88	0.50	3.00	1.13	0.790	0.051	0.159	1348
POM 3	0.50	1.58	0.50	3.00	1.42	0.488	0.129	0.383	1307
POM 4	0.50	2.06	0.50	3.00	0.94	0.797	0.051	0.152 (MgO)	1332
POM 5	0.50	2.00	0.50	3.00	2.08	0.48	——	0.52	1329
POM 6	0.50	1.75	0.50	3.00	1.70	0.48	0.07	0.45	1322
POM 7	0.50	1.30	0.50	3.00	1.00	0.48	0.36	0.26	1317
POM 8	0.50	0.96	0.50	3.00	0.48	0.48	0.52	——	1356
							0.5 K_2O, 0.3 SiO_2		
P(K6S)M 1	0.50	1.58	0.40	3.00	1.40	0.50	0.125	0.375	1323
							K_2O, SiO_2		
P(KS)M 1	0.69	1.85	0.46	3.00	1.60	0.50	0.125	0.375	1296
P(KS)M 2	0.53	1.98	0.48	3.00	1.19	0.80	0.05	0.15	1340
					AlF_3			AlF_3	
POA 1	0.50	3.00	0.17	3.00	0.69	1.00	——	——	1362
POA 2	0.50	2.40	0.23	3.00	1.13	0.50	0.125	0.375	1333
					K_2SiF_6			$\frac{1}{3}$ K_2SiF_6	
POKs 1	0.26	2.63	0.54	3.00	0.43	0.50	0.125	0.375	1309
PKs 1	0.19	3.37	0.56	3.00	0.75	0.50	——	0.50	1320
PKs 2	0.19	3.37	0.56	3.00	0.47	0.80	——	0.20	1355
					K_3AlF_6			$\frac{1}{2}$ K_3AlF_6	
POKa 1	0.10	2.40	0.25	3.00	0.47	0.50	0.125	0.375	1300
PKa 1	——	3.00	0.33	3.00	0.67	0.50	——	0.50	1315
PKa 2	——	3.00	0.33	3.00	0.42	0.80	——	0.20	1350

* This paper is an abstract of the summary of the work published on *Kogyo Kagaku Zasshi* (*The Journal of the Society of Chemical Industry, Japan* or *The Journal of the Chemical Society of Japan, Industrial Chemistry Section*) from 1943 to 1948 and *Kogyo Butsuri Kagaku* (*Industrial Physical Chemistry*), 1948, No. 1, 108–119, and 1949, No. 2, 179–203.

(1) Tokiti Noda and Sachio Sugiyama, *Journ. Soc. Chem. Ind., Japan*, **46**, 921 (1943), *Suppl. Bind.*, 193 B (in English).

(2) T. Noda and S. Sugiyama, *ibid.*, **46**, 1082 (1943), *Suppl. Bind.*, 225 B; **47**, 320 (1944).

(3) T. Noda and S. Sugiyama, *ibid.*, **47**, 623 (1944).

(4) T. Noda and S. Sugiyama, *ibid.*, **47**, 625 (1944).

P(Ks) phlogopite-potassium silicofluoride[5]
POKa phlogopite-orthoclase-potassium aluminofluoride[6]
PKa phlogopite-potassium aluminofluoride.[6]

The "quenching" method was used for the measurement. Raw materials used were chemically pure silicium oxide, magnesium oxide, aluminium oxide, magnesium oxide, potassium carbonate and fluorides. The mixture of a definite proportion of these raw materials was enclosed in a small platinum tube and suspended with a platimum wire in a platinum ribbon resistance furnace and heated to 1420°~1430°. After completely melted, the specimen was cooled to a desired temperature and maintained at the temperature for one hour or more and quenched. The experimental results are shown in Table 1. Temperature of crystallization means the temperature where mica crystals begin to appear.

In general, good results were obtained with compositions which contained large concentrations of phlogopite. In POM group, POM2 gave the best reusult. As the melt of orthoclase has a high viscosity and solidifies into hard glass, its presence in large amounts is not favorable. Melts of P(K6S)M and P(KS)M compositions gave softer and better splitting mica than POM composions. Better tesults were obtained with phlogopite-fluoride two-component compositions. Among various fluorides tested, potassium silicofluoride gave the best result and magnesium fluoride the next.

The velocity of crystallization of several compositions was measured by the same method as the measurement of the temperature of crystallization. Specimens maintained at a definite supercooled temperature for various periods were quenched. The velocity was calculated from the largest dimension of produced crystals. The results are shown in Table 2.

Table 2

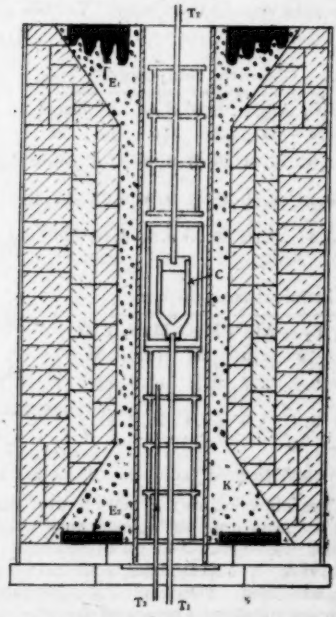
Specimen	Temp. of crystn. °C.	Degree of supercooling °C.	Max. velocity of crystn. mm./min.	Approx. no. of nuclei, no./3 mm².
POM 3	1307	6	0.12	——
POM 2	1348	3	0.08	one to several
		6	0.16	10 to 30
		10	0.47	several tens
		20	0.40	many
P(KS)M 1	1296	3	0.13	——
P(KS)M 2	1340	3	0.10	4 to 8
		6	0.18	20 to 40
		10	0.59	many

The velocity of crystallization increases to a maximum point and then begins to decrease, as the degree of supercooling increases. The number of nuclei increases rapidly with the degree of supercooling. Therefore, it is desirable to maintain a minimum degree of supercooling with sacrifice of the velocity, in order to produce as large crystals as possible in a given space.

(5) S. Sugiyama, *Journ. Soc. Chem. Ind., Japan*, **48**, 14 (1945).
(6) S. Sugiyama, *ibid.*, **48**, 15 (1945).

Experiments on the Formation of Large Crystals

A large number of the experiments were performed in a small scale with a platinum resistance furnace and in a somewhat larger scale with a cryptol resistance furnace of about 1kg. capacity. A large variety of compositions were tested, but the formation of large crystals resulted with the compositions in the neighborhood of POM 2. From PKs 2 easily splitting mica crystals were produced. Sometimes, calcined silica, alumina, and magnesia were mixed with potassium carbonate and heated to about 900° to drive off carbon dioxide. The heated mass was powdered and mixed with magnesium fluoride, pressed and filled in the crucible. In other cases, calcined oxides, potassium carbonate and magnesium fluoride were mixed and pressed without the preliminary heating. The filled crucible was covered with a lid and put in a larger grog crucible. The space between the two crucible was filled with granulated grog. The assembled crucible was set in the proper position of the furnace. A general section of the furnace is shown in the figure. The crucible was heated slowly to about 900° and from 900° to 1420~1450° as quickly as possible to avoid the loss of fluorine. When the charge in the crucible was melted completely, it was cooled to 1400°~1380° and from that temperature to 1300° slowly at the rate of 2~3° per hour. After passing this temperature



Vertical section of the cryptol resistance furnace: T_1,T_2,T_3, thermocouple; C, graphite crucible; E_1, E_2, iron electrode; K, cryptol.

range, the current was cut off. After the furnace was cooled down, the crucible was taken out. The temperature of the charge was measured by thermocouples continuously and by an optical pyrometer frequently.

Three methods were tested to start the crystallization from one point.

(a) The upper part of the melt was kept at higher temperature, so that nuclei would be formed at the cone-shaped bottom and grow upward. This method was used most frequently. It was somewhat difficult to control the temperature gradient as desired with the cryptol furnace.

(b) An inner graphite crucible, whose horizontal section was triangular or fan-shaped, was placed in the melting crucible. The inner crucible had a small hole at the corner of the bottom. When the melt was cooled, the part between the inner and the outer crucibles solidified first. The peeped crystal from the small hole of the inner bottom might have become a starting point for crystallization of the inner melt. Comparatively large crystals were formed in the small inner space.

(c) A platinum plate attached on a water-cooled brass pipe was dipped in the melt. Crystals attached rapidly on the plate. The plate was then raised very slowly, as a single crystal grew vertically downward.

Although the latter two methods were tried but not many times, they seemed to be promising.

Originally, high aluminous grog cruibles were used. With longer contact with the melt, these crucibles were attacked seriously. Various kinds of crucibles obtained in the market were tested. Sintered alumina crucible resisted very well, but it was not used because of its high cost. In a large number of experiments, artificial graphite crucibles were used. They can be used repeatedly, since the solidified mass separates easily from the crucible. But graphite makes a reducing atmosphere in the crucible and changes the composition of the melt more easily than neutral atmosphere. This reducting atmosphere colors the mica block gray, therefore it is desirable to operate in neutral or oxidizing atmosphere.

It was observed that aluminium oxide came from aluminous or grog crucible reacted with the melt and precipitated magnesium spinel. Spinel was very stable in the melt. Several compositions of the MgO-Al_2O_3-SiO_2 system were tested for corrosion. Specimens of spinel accompanying small amount of periclase and forsterite were very stable. Good sintered specimens of mullite or forsterite-periclase resisted sufficiently good, too.[7][8]

Properties of Synthetic Mica

The chemical composition and the optical properties of synthetic mica are shown in Table 3.[9]

The synthetic mica is stable at high temperatures up to 1100° and begins to decompose at 1200° by liberating small amounts of gas.[10][11] The liberated gas contained silicium tetrafluoride in large amounts.[11]

Preparation of Various Kinds of Mica by Isomorphous Substitution

Various kinds of mica were prepared by substituting the tetrahedral aluminum, octahedral magnesium and cubo-octahedral potassium of phlogopite by their crystal chemical equivalent elements.

A. Substitution of Tetrahedral Aluminium

(*a*). **Boron-phlogopite.**[12]—The mixture of 0.50 K_2O, 1.50 MgO, 1.50 MgF_2, 0.50 B_2O_3, 0.05 Al_2O_3, 3.00 SiO_2 melted clearly at 1250° and

Table 3

Specimen	Chemical composition: SiO_2 %	Al_2O_3 %	MgO %	K_2O %	F %	Total %	Optical properties: Refractive Index α	β	γ	$\gamma-\alpha$	Optical angle, 2E	Chemical formula
1	42.01	16.84	26.61	8.66	5.70	99.81	1.522	1.553	1.554	0.029	19°	$(O_{0.7}F_{1.3})K_{0.8}Mg_{2.8}Al_{0.4}(Al_{1.0}Si_{2.9}O_{10.0})$
2	40.73	18.50	25.41	9.20	6.03	99.87	1.544	1.564	1.566	0.029	20°	$(O_{0.6}F_{1.4})K_{0.8}Mg_{2.7}Al_{0.4}(Al_{1.2}Si_{2.8}O_{10.0})$
3	43.44	13.90	26.95	9.68	6.16	100.12	1.513	1.539	1.540	0.027	22°	$(O_{0.6}F_{1.4})K_{0.9}Mg_{2.9}Al_{0.3}(Al_{0.9}Si_{3.1}O_{10.0})$

Table 4

	Chemical composition: SiO_2 %	B_2O_3 %	Al_2O_3 %	MgO %	MgF_2 %	K_2O %	Chemical formula	Optical properties: α	β	γ	$\gamma-\alpha$	2E	Specific gravity
(1)	43.5	9.4	2.7	21.1	14.3	11.1	$(F_{1.80}O_{0.19})K_{0.9}Mg_{2.97}Al_{0.10}(Al_{0.10}B_{1.07}Si_{2.86}O_{10.00})$	1.506	1.526	1.529	0.020	13°	2.730
(2)	43.4	9.8	1.5	19.8	15.2	11.2	$(F_{1.93}O_{0.05})K_{0.95}Mg_{2.94}Al_{0.10}(B_{1.12}Si_{2.85}O_{10.00})$	1.505	1.521	1.522	0.017	27°	2.731
(2′)								1.501	1.526	1.518(calc.)			

(1) melted in grog crucible, (2) melted in platinum crucible, (2′) calculated[13]

(7) T. Noda and Masao Konno, *Journ. Ceramic Soc., Japan*, **57**, 25 (1949).

(8) T. Noda and Kiyoshi Mori, *ibid.*, **57**, 104 (1949).

(9) T. Noda and S. Sugiyama, *Journ. Soc. Chem, Ind., Japan*, **46**, 760 (1943), Suppl. Bind., 162 B.

(10) T. Noda and Koichi Aoki, *ibid.*, **51**, 7 (1948).

(11) T. Noda and Toru Matsushita, *ibid.*, **51**, 83 (1948).

(12) T. Noda, Nobutoshi Daimon and Hitoshi Toyoda, *ibid.*, **47**, 449 (1944).

(13) T. Noda and Daimon, *Journ. Electrochem. Soc., Japan*, **14**, 125 (1946).

began to crystallize at 1150°. The chemical compositions and the optical properties of the produced mica crystals are as shown in Table 4.

(*b*). **Zinc-mica.**[14]—To the mixture of 0.50 K_2O, 1.50 MgO, 1.50 MgF_2, 0.50 ZnO, 0.05 Al_2O_3, 3.50 SiO_2 was added excess ZnO to cover the loss by evaporation. The mixture was melted in a grog crucible and cooled. Comparatively good mica crystals separated out. The chemical composition of the mica is:

SiO_2, 41.58%; ZnO, 7.03%; Al_2O_3, 9.06%, MgO, 17.83%; MgF_2, 14.11%; K_2O, 10.75%.

The chemical formula is $F_{2\cdot0}K_{1\cdot0}Mg_{2\cdot9}Zn_{0\cdot2}(Zn_{0\cdot2}Al_{0\cdot8}Si_{3\cdot0}O_{10\cdot0})$.

(*c*). **Beryllium-mica.**[14]—The mixture of 0.50 K_2O, 1.90 MgO, 1.10 MgF_2, 0.50 BeO, 0.05 Al_2O_3, 3.00 SiO_2 melted at about 1350°. Mica crystals separated by cooling.

(*d*). **Iron-mica.**[14]—The mixture of 0.50 K_2O, 1.50 MgO, 1.50 MgF_2, 0.50 Fe_2O_3, 0.05 Al_2O_3, 3.00 SiO_2 crystallized out black to brown mica.

B. Substitution of Cubo-octahedral Potassium[15]

(*a*). **Natrium-mica.**—The mixture of 0.50 Na_2O, 1.50 MgO, 1.50 MgF_2, 0.50 Al_2O_3, 3.00 SiO_2 melted at about 1325°. Mica crystals obtained were small.

(*b*). **Calcium-mica.**—The mixture of 0.50 CaO, 1.50 MgO, 1.50 MgF_2, 0.50 Al_2O_3, 3.00 SiO_2 melted at about 1200°. Rapid cooling resulted glass. By slow cooling, minute mica crystals were obtained.

(*c*). **Strontium-mica.**—The mixture of 0.50 SrO, 1.50 MgO, 1.50 MgF_2, 0.50 Al_2O_3, 3.00 SiO_2 melted at about 1450°. Small mica crystals were obtained.

(*d*). **Barium-mica.**—The mixture of 0.50 BaO, 1.50 MgO, 1.50 MgF_2, 0.50 Al_2O_3, 3.00 SiO_2 melted at about 1400°. Mica crystals obtained were large, but brittle and difficultly splitting. The mixture of 1.00 BaO, 1.50 MgO, 1.50 MgF_2, 1.00 B_2O_3, 2.00 SiO_2 melted at about 1200°. By rapid cooling glass formed, by slow cooling, small mica crystals crystallized.

C. Substitution of Octahedral Magnesium and Preparation of Colored Mica[16]

The following mixtures shown in Table 5 produced mica crystals. (The temperature of melting by reaction and the colors of the produced mica crystals are also listed).

Table 5

Cemical composition of mixtute	Temp. of melting °C.	Color of mica
0.5 K_2SiF_6, 1.5 MgO, 1.5 MnO_2, 0.5 Al_2O_3, 2.5 SiO_2	1350	brown
0.5 K_2SiF_6, 1.5 MgO, 1.5 FeO, 0.5 Al_2O_3, 2.5 SiO_2	1350	brack
0.5 K_2SiF_6, 2.75 MgO, 0.25 $NiCO_3$, 0.5 Al_2O_3, 2.5 SiO_2	1400	yellowish green
0.5 K_2SiF_6, 2.75 MgO, 0.08 Co_3O_4, 0.5 Al_2O_3, 2.5 SiO_2	1400	pink
0.5 K_2SiF_6, 2.75 MgO, 0.09 Cr_2O_3, 0.5 Al_2O_3, 2.5 SiO_2	1400	yellow
0.5 K_2SiF_6, 2.75 MgO, 0.125 NH_4VO_4, 0.5 Al_2O_3, 2.5 SiO_2	1400	
0.5 K_2SiF_6 2.0MgO, 1/3 Co_3O_4, 0.5 B_2O_3, 2.5 SiO_2	1200	blue
0.5 K_2O, 2 LiF, TiO_2, 0.5 B_2O_3, 3 SiO_2	1100	faint pink
BaF_2, 2 MgO, 0.5 Li_2CO_3, 0.5 B_2O_3, 3 SiO_2	1100	white
SrF_2, 2 MgO, 0.5 Li_2CO_3, 0.5 B_2O_3, 3 SiO_2		white
CaF_2, 2 MgO, 0.5 Li_2CO_3, 0.5 B_2O_3, 3 SiO_2		white

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Nagoya

(14) T. Noda and N. Daimon, *Journ. Soc. Chem. Ind., Japan*, **49**, 125 (1946).

(15) T. Noda, N. Daimon and Utai Songkram, *Journ. Ceram. Soc., Japan*, **52**, 95 (1944).

(16) N. Daimon, Not yet published.

On the Porperties of Water Surface in Contact with Various Vapors*

By Toshio IKEDA and Tokurô OZAKI

(Received December 6, 1949)

The Experimental Procedure and the Results.—The surface tension of water in various vapors was measured by the drop-volume method. The experimental equipment is shown in Fig. 1. The thick capillary polished flat at one end, where the water drop hangs, was joined to a burette filled of distilled water by a thick rubber tube for vacuum use, and to the middle of the tube a screw cock was attached in order to control the rate of dropping. The capillary end is held air-tight in the thick glass globe by a large coutchouc cork through which a glass tube is reserved for sending the air saturated with the vapor to be investigated into the glass globe, and the pressure in the globe may easily be regulated by a pump.

After sending the air saturated with the vapor into the glass globe for about 5 min., the dropping of water is started at the constant rate. From the observations of fifty drops we

* "International Critical Table" IV, 436; Landolt-Börnstein, "Phys-chem. Tabellen" Bd. I, 208, 243 (1923); Erg. Bd. I, 149, 154 (1927); 154, 168 (1931).

obtain the mean volume of an water drop, v cc., and the average life of one drop, τ.

The behaviors at 20° are shown in Fig. 2-a and -b. As it is seen there, the surface tension of water is affected markedly by the sort of vapor in contact, which are arranged in increasing order, that is : in air < benzyl chloride < carbon bisulfide < *n*-hexane, carbon tetrachloride < benzene < ethylene dichloride < chloroform < isoamyl alcohol < ethyl acetate < isoamyl acetate < ethyl ether.

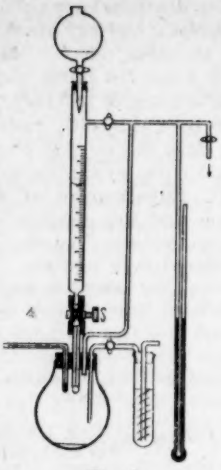


Fig. 1.

The "Ageing" of the Water Surface and its Mechanism.—As is seen in Fig. 2, the water surface developed afresh has its maximum value of surface tension which diminishes to the equilibrium value with time, about 6 seconds in general. Therefore, the aging period of the water surface must be about 6 seconds, which is extremely short as compared with that of solution which demands more than 30 min. or even several hours. In other words, the time demanded to attain the adsorption equilibrium of vapor on the water surface is extremely short as compared with that of the solute in solution. This may be ascribed to the fact that the movement of the molecules in gas phase is by far free as compared with that in solution.

The Vapor-Water Interfacial Tension and the Relation to "Antonoff's Rule".—The surface tension of water (W)-drop in vapor

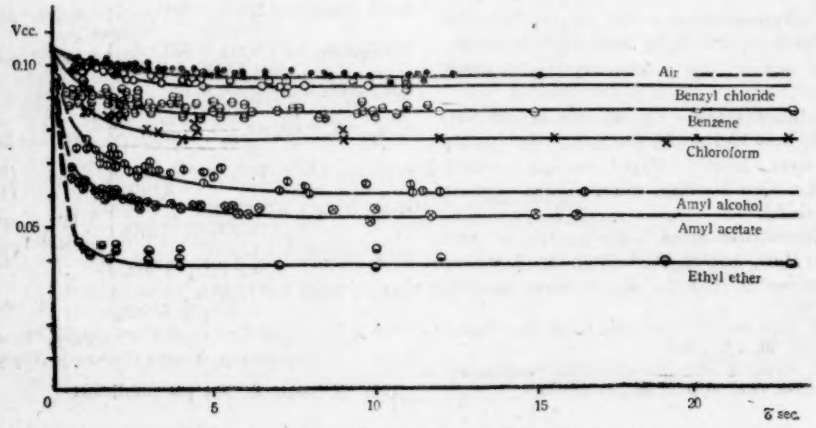


Fig. 2 a.—v_{W-G}, Drop volume of water in vapor.

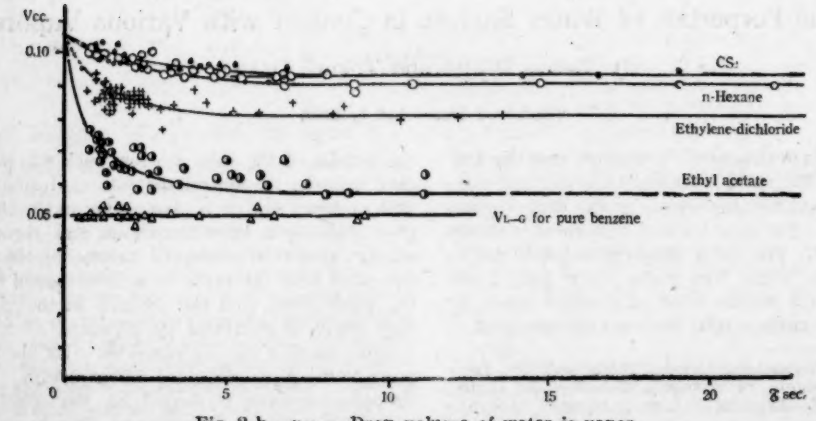


Fig. 2 b.—v_{W-G}, Drop volume of water in vapor.

(G), γ_{W-G}, is calculated by the formula

$$\gamma_{W-G}=\frac{v\cdot\rho\cdot g}{2\pi ar} \quad (1)$$

(taking the contact angle of water for zero) where v is the volume of a water-drop, ρ the density of water, g the acceleration of gravity, r the outer radius of capillary used and a is a correcting constant to be determined by experiment. In our experiment, $r=0.338$ cm., $a=0.610$. The results are shown in Table 1 where v_c (column 2) is the observed volume of one drop in the constant region after its ageing period, about 6 sec., γ_{Z-G} is the surface tension of the "pure" organic liquid in contact with air (with its vapor G), and $\gamma_{W'-L'}$ is the interfacial tension at the interface of water-liquid saturated with each other.

Table 1 (20°C.)

Name of G or L.	v_c, cc.	γ_{W-G} dyne /cm.	γ_{L-G} dyne /cm.	$\gamma_{W'-L'}$ dyne /cm.	$\gamma_{W'-L'}+\gamma_{L-G}$ dyne /cm.
Air	0.096	72.6	——	——	——
Benzyl chloride	0.093	70.5	39.9*	30.5	70.4
Carbon bisulfide	0.092	69.5	33.58	49.3	82.88
n-Hexane	0.090	68.0	17.34	50.96	68.30
Carbon tetrachloride	0.090	68.0	25.68	43.6	69.28
Benzene	0.085	64.2	28.88	34.96	63.84
Ethylene dichloride	0.080	60.5	31.1	29.2**	(60.3)
Chloroform	0.076	57.5	26.0	31.8	57.8
iso-Amylalcohol	0.060	45.5	23.8	5.0	28.8
Ethyl acetate	0.056	42.5	23.6	6.7	30.3
iso-Amyl acetate	0.053	40.0	24.08	10.8	34.88
Ethyl ether	0.038	28.5	17.10	10.7	27.8

* Observed by capillary height method.

** This value was estimated ftom $\gamma_{W'-L'}=37.2$ dyne/cm. for ethylene dibromide at 20°. In many cases, the value of $\gamma_{W'-L'}$ for aliphatic halogenide decreases by about 8 dynes on replacing the bromine atom by chlorine.

Comparing the columns 3 and 6, we shall see the excellent agreements between them except carbon bisulfide, alcohols, acetic esters. These agreements can not be considered accidental. Thus we may take the following rule

$$\gamma_{W-G}=\gamma_{W'-L'}+\gamma_{L-G}. \quad (2)$$

Using similar expression, the "Antonoff's rule" is expressed in

$$\gamma_{W'-A}=\gamma_{W'-L'}+\gamma_{L'-A}, \quad (3)$$

where W′ and L′ denote the phase W and L saturated with each other, and A the air in contact with W′ or L′. Since the three phases W′, L′ and A are in equilibrium, and since just the surface layer of water-drop in contact with the vapor of L is assumed to be saturated with L, so that we may put $\gamma_{W-G}=\gamma_{W'-A}$. And since the surface tension of organic liquids are not affected exceedingly by whether they are wet or dry,[1] the law (2) may be reduced to the "Antonoff's rule" itself.

As regards the lower membered acetic esters and alcohols, the relation may be expressed as follows:

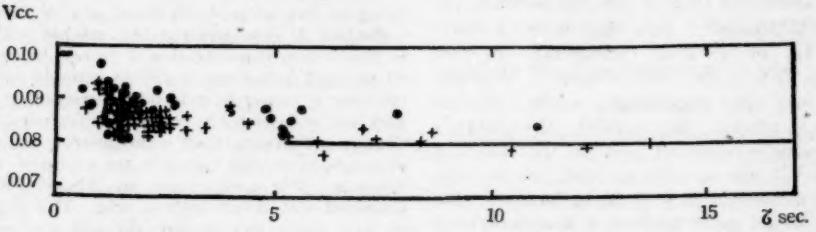


Fig. 3.—The effect of pressure on v_{W-G} (G=ethylene dichloride): + under ordinary pressure, ● under 10~15 cm.Hg.

$$\gamma_{W-G}>\gamma_{W'-L'}+\gamma_{L-G}. \quad (4)$$

On the other hand, the relation for carbon bisulfide is

$$\gamma_{W-G}<\gamma_{W'-L'}+\gamma_{L-G}. \quad (5)$$

The Effects of Pressure.—On decreasing the vapor pressure, the increase in the surface tension of warer, γ_{W-G}, so that in v, might be expected owing to diminishing the attraction of molecules of vapor outside on the surface molecules of water. The observations were made about ethylene dichloride under reduced pressure of the system down to 10 cm.Hg, which corresponds to 0.8 cm.Hg in partial pressure. The increase of v by 0.004 cc. was found with difficulty even at $\tau<6$ sec., but the prolongation of the ageing period up to 10 seconds, which was 6 sec. under ordinary pressure, so that the effect of pressure on v, if any, must appear under sufficient low pressure.

Summary

The surface tension of water in various vapors were measured by the drop-volume method. As a result of the experiment, it was found that the "Antonoff's rule" holds good with some exceptions. In any vapors, a remarkable, but short ageing of water surface was found, which was 6 seconds in general, and which is prolonged by reduced pressure.

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(1) W.D. Harkins, "The 6th Colloid Symposium Monograph," 17 (1928).

Separation of a Small Amount of Titanium from Iron by Ion-Exchange Resin

By Yukichi YOSHINO and Masuo KOJIMA

(Received December 10, 1949)

Introduction

In determining a small amount of titanium, the colorimetric method with hydrogen peroxide[1] has been most commonly used. But, if a sample contains much iron, the color of ferric ion intensifies that of the test solution.

W.F. Hillebrand[2] says that 0.1 g. of Fe_2O_3 in 100 cc. of solution corresponds to 0.02 per cent TiO_2 in the same volume of solution.

To avoid this interference, various devices have been offered. For example, the addition of the same amount of iron to the standard solution[3] is the simplest method. In the case when iron content is very high, however, this method would prove ineffective in determining titanium. P. Faber[4] recommended the addition of phosphoric acid to both the standard and the test solution in order to neutralize the effect of iron. However, since phosphoric acid weakens the yellow tint to some extent, the use of this method is not always desirable when the amount of titanium is very small.

For accurate analysis, therefore, sepatation of titanium from iron before the color development seems to be the most desirable. For such a purpose, the separation of iron as ferrous sulfide in presence of tartaric acid[5] has been in the most common use. For the satisfactory employment of this method, however, the double precipitation of ferrous sulfide is necessary, because a part of titanium is apt to coprecipitate with it. Moreover, the tartaric acid must be completely decomposed before development of the color.

The authors have studied the method of separation of both elements using an ion-exchange resin and found that even a large amount of iron could be removed as ferricyanide complex ion as described in the following.

Experimental

Apparatus and Reagent.—The cation-exchanger used was one of commercial phenolsulfonic acid polymers and between 30 and 70 mesh of size. Five or ten grams of the resin were conveniently equipped in a 50 cc. burette. The standard solution of ferric ion was prepared from Merck's ferric sesquichloride and that of titanium from Kahlbaum's titanium dioxide after bisulfate fusion.

Determination Method of Titanium.—In the experiment, the standard solutions of both ions were mixed together in various proportions, then following two ways of treatment were studied.

Method 1.—On treating the sample solution, in which iron concentration is rather high, with 50 per cent potassium or sodium cyanide solution, the iron is converted into both ferricyanide complex ion and ferric hydroxide percipitate, while titanium coprecipitates quantitatively as white titanium hydroxide owing to the excess of alkali cyanide. The precipitates are filtered off and dissolved with dilute sulfuric acid. This is diluted with water and passed through the column of resin previously saturated with hydrogen ion. Then, the resin is washed with about 200 cc. of 2*N*-KCN solution at the rate of 1 cc. per minute or less. The adsorbed iron is gradually eluted out as ferricyanide complex, while titanium remains without change. After washing the column thoroughly with water, adsorbed titanium is eluted with from 100 to 200 cc. of 10 per cent sulfuric acid. The aliquot portions of the eluent are used for colorimetric determinations of titanium as well as remaining iron. The results are shown in Table 1.

Table 1

Expt.	Ions	Taken, mg.	Found, mg.	Error, mg.
1	Ti^{++++}	0.12	0.12	0
	Fe^{+++}	50.2	2.3	—
2	Ti^{++++}	0.68	0.68	0
	Fe^{+++}	67.2	0.3	—

If the concentration of iron is relatively low, all the iron is apparently converted into complex ion by previous treatment with the excess of concentrated potassium cyanide solution while titanium forms the precipitate. In such a case, a little dilute sulfuric acid just enough to dissolve the precipitate is added very cautiously and the solution is passed through the column of resin. After elution with 10 per cent sulfuric acid, titanium is determined as before. Table 2 shows the results of such experiments.

Table 2

Expt.	Ions	Taken, mg.	Found, mg.	Error, mg.
1	Ti^{++++}	0.48	0.45	−0.03
	Fe^{+++}	0.88	trace	—
2	Ti^{++++}	0.68	0.66	−0.02
	Fe^{+++}	0.88	trace	—

Method 2.—Various mixed solution of iron and titanium are passed through the resin

(1) A. Weller, *Ber.*, **15**, 2592 (1882).
(2) W.F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 160 (1919).
(3) W.A. Noyes, *Journ. Anal. App. Chem.*, **5**, 39 (1891).
(4) P. Faber, *Chem. Zeit.*, **31**, 263 (1906).
(5) R. Fresenius, *Z. anal. Chem.*, **1**, 69 (1862).

without any previous treatment. The adsorbed iron is eluted out with from 300 to 500 cc. of 2*N*-NaCN solution as slowly as 1 cc. per minute or less. The elution and determination of titanium are conducted as described above. The results are listed in Table 3.

Table 3

Expt.	Ions	Taken, mg.	Found, mg.	Error, mg.
1	Ti^{++++}	0.68	0.66	—0.02
	Fe^{+++}	0.88	0.08	—
2	Ti^{++++}	0.68	0.71	+0.03
	Fe^{+++}	8.78	0.16	—
3	Ti^{++++}	0.68	0.68	0
	Fe^{+++}	67.2	0.25	—

The results obtained by both Methods 1 and 2 seem to be satisfactory for the colorimetric determination of a small amount of titanium in a sample rich in iron.

Determination of Titanium in Limonite.—As an example of practical application of the method, the titanium content in the limonite from Asahida mine, Kumamoto Pref., Kyushû is determined. The spectroscopic analysis of the sample showed the presence of the following minor constituents.

Al, Be, Ca, K, Li, Mg, Mn, Na Si, Ti, V.

Of these, the content of vanadium was previously determined by E. B. Sandell's colorimetric method[6] and obtained the value of 0.012 per cent as V. The iron content was 74.51 per cent as Fe_2O_3. Therefore, the test solution was prepared according to the following procedure. About 1 gram of the powdered sample was weighed and fused with sodium carbonate and the fused mass was leached with water. The residue was dissolved in a small volume of hot 10 per cent sulfuric acid and diluted to 250 cc., of which 50 cc. was used for titanium determination according to the Method 1.

To make sure, we took another portion of the test solution and separated iron as ferrous sulfide by the ordinary hydrogen sulfide method and determined titanium colorimetrically. The results of both experiments were in good agreement as indicated in Table 4.

Table 4

Method of Separation	Titanium Content, % TiO_2
Resin method	0.207
H_2S method	0.197

(6) E.B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **5**, 336 (1936).

Discussion

As cation exchange resin is not resistant enough against alkaline solution, its repeated use will result in the decrease of exchange capacity and will not be desirable. By reason of that, Method 1 which requires less alkali cyanide solution as an eluting agent seems to be more preferable to Method 2 in case of a sample rich in iron.

Summary

Separation of a small amount of titanium from iron with cation exchange resin was studied using alkali cyanide solution as eluting agent of iron. Successful results were obtained even in case of high iron concentration. This method enables us to remove the interfering effect of the iron on titanium colorimetry with hydrogen peroxide.

As an examle of practical application, this method was tried in determining the titanium content of a limonite. The result agreed with that of the ordinary method of separation.

The authors, hereby, wish to express their hearty thanks to Prof. Eiiti Minami at the University of Tokyo for his kind guidance and encouragement. And authors also appreciate Messrs. M. Honda, H. Kakihana and M. Tanaka's advices, which proved to be of tremendous help in performing these studies.

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Studies on Foams. IV. The Effect of Electrolyte on the Foam Formation of Congo Red Solution

By Masayuki NAKAGAKI

(Received December 12, 1949)

The foams may be classified into two groups, namely hydrophobic or less stable foam and hydrophilic or more stable foam. The less stable foam is obtained by the aqueous solutions of alcohols, fatty acids and electrolytes and it has shorter foam duration than 30 seconds. The more stable foam is obtained by soaps, dyes, proteins and various detergents. According to O. Bartsch[1] the less stable foam behaves like the negatively charged hydrophobic colloid and easily unstabilized by the addition of electrolyte, while the more stable foam hardly affected by the electrolyte. The present author considers, however, that such a conclusion is not quite correct, especially in the case of the more stable foam. In order to study on this problem the foam formation of congo red solution in the existence of electrolytes has been measured.

(1) O. Bartsch, *Kolloid-Beih.*, **20**, 1 (1925).

The foam formation was determined by the shaking test. Twenty cubic centimeters of solution was taken into a test tube of 40 cc. in capacity and 1.8 cm. in diameter, providing a glass stopper. This was shaken up and down for 30 seconds at the rate of 3 times per second and at the amplitude of 25 cm. Soon after the shaking, the height of the foam zone becomes maximum (usually less than 5 seconds). The height of the maximum foam zone A_m is read, which is taken as a measure of foaminess of the solusion. The foam, then, gradually collapses untill at last a part of free liquid surface appears. Let the time required for the appearance of free liquid surface be t, which is taken as the measure of the foam duration. The change of the height of foam zone with time is also recorded. The strength of foam, τ, is calculated as the reciprocal of the collapsing velocity of foam zone for the initial 30 seconds, thus,

$$\tau = \frac{30}{A_m - A_{30}} \left(\frac{\text{sec.}}{\text{cm.}}\right) \quad \text{for} \quad t > 30 \text{ sec.}$$

where A_{30} denotes the foam height read at 30 seconds after the the maximum height of foam zone is attained.

The stock solution of dye has been prepared in the following manner. Four grams of congo red (Merck's sample) was boiled with distilled water for several minutes and then adjusted accurately to one litre in volume after cooling. Just before the measurement, this solution was diluted with distilled water or some electrolyte solution untill the concentration of dye became 3.20 grams per litre. In order to avoid the effect of aging of solution, measurements have been undertaken just at one week after the preparation of the stock solution.

The general feature of the change of foam formation of congo red solution by the addition of sodium chloride is shown in Fig. 1. A prominent maximum is found in the curve of the foam duration at relatively low concentration of electrolyte, and also a maximum is seen in the curve of foam strength, while no maximum is observed in the curve of the foaminess. It is usually said that the foaminess and foam duration or foam strength of a solution are independent of each other. As an example the solutions of saponin and n-butyl alcohol are often cited, the former produces a more stable but less voluminous foam than the latter. This example, however, is not suitable in this case, for the foam stability of saponin solution may be due to some special reason, such as the formation of an insoluble film. In fact, foaminess and foam duration change, in most cases, similarly with each other, by the change of concentration. This is valid as far as the viscosity of solution is not extremely large, as discussed in the previous paper[2] on the less stable foams. This does not seem, however, to be true for the finely dispersed, long lasting foam.

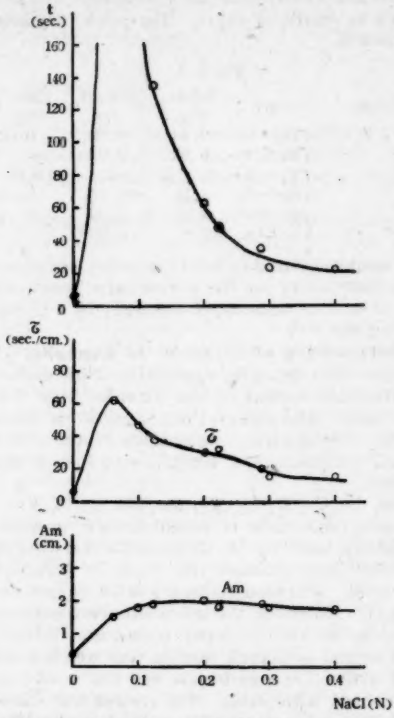


Fig. 1.—The effect of NaCl on the foam formation of congo red solution.

Such a steep maximum in foam duration of 3.20 g./l. congo red solution is also found by the addition of $NaNO_3$, NaOH, HCl, and $BaCl_2$. It is notable that a good peptization agent NaOH, a strong precipitation agent $BaCl_2$, and an acid HCl behave in the same manner as NaCl and $NaNO_3$, though the concentration for the maximum of foam duration is different from each other. As it is well known, acid precipitates blue congo acid from the solution of congo red. The concentrations of these electrolytes at the maximum point of foam strength are shown in Table 1.

One plausible explanation of the maximum of foam formation may be the peptization of dye particles by the electrolyte. Wo. Ostwald [3] and R. Tanaka[4] found the phenomenon that the congo acid is peptized by the addition of small amount of electrolyte. W. Schramek and E. Götte[5] stated from diffusion data, and T. H. Morton[6] from ultra-filtration experiments,

(2) M. Nakagaki, This Bulletin, **21**, 30 (1948).

(3) Wo. Ostwald, *Ber.*, **62**, 1194 (1929).
(4) R. Tanaka, *Kolloid-Z.*, **54**, 156 (1931).
(5) W. Schramek and E. Götte, *Kolloid-Beih.*, **34**, 218 (1932).
(6) T. H. Morton, *Trans. Faraday Soc.*, **31**, 262 (1935).

that the particle size of dye became minimum by the addition of small amount of electrolyte. C. Robinson,[7] E. Valkó[8] and S. M. Neale,[9] however, recognized no minimum point on their curves of particle size to concentration of added electrolyte. The same conclusion was obtained by the present author. It will be reported in another paper. After all, peptization may be an action to disperse a precipitated mass into colloidal particles, scarcely affecting the size of particles already dispersed in sol state.

In spite of little change of particle size, the foam formation shows a steep maximum with the addition of the small amount of electrolyte. This is explained by the idea presented in the preceding paper,[10] that the foam formation is mainly predominated by the separately dispersed ions rather than the portion of dye dispersed in colloidal aggregates, and that the surface chemical porperties of dye ions are determined by the balance of its hydrophilic and hydrophobic character. The addition of electrolyte decreases the affinity of the polar part of dye ions to solvent, and this results in the increase of the surface activity of solute. In fact, the specific surface tension to water measured by du Nouy's tensiometer for 3.20 g./l. of congo red solution decreases from 0.98 for pure dyestuff solution to 0.96 for solution containing 0.48 *N* of sodium chloride. The increase of surface activity, from which the increase of foam formation is explained, is regarded as a presage of salting out. When the concentration of electrolyte is further increased, the affinity of polar group of dye ion to solvent becomes weaker, till the dye ions coagulate and precipitate from the solution. The decrease of foam duration may be related to this process. The coagulation value will have a certain connection with the electrolyte concentration of maximum foam strength, as a measure of the ability of electrolyte to enfeeble the affinity between dye and solvent.

Table 1
Maximum Foam Formation and Coagulation Value.

Electrolyte	Concn. of electrolyte for max. foam strength, *N**.	Coagulation value**, *N*.
NaOH	0.17	0.73
$NaNO_3$	0.11	1.07
NaCl	0.062	0.71
$BaCl_2$	0.0043	0.0056
HCl	0.0028	0.0043

* Concentration of congo red is 3.20 g./l.
** Concentration of congo red is 2.00 g./l.

The coagulation value of 2.00 g./l. congo red solution has been measured, and the result is cited in Table 1. Since the coagulation of congo red is a "Slow Coagulation," the coagulation value is varied with time, and coagulation is observed in fairly dilute solution of electrolyte after a long time. In this report, the coagulation value is defined as the minimum concentration of electrolyte necessary to make solution turbid after 24 hours. Comparing the concentration of electrolyte for maximum foam strength with the coagulation value, the general drift coincides with one another.

Summary

The changes of foaming power of the solution of congo red by the addition of electrolytes have been estimated. There is a prominent maximum in the foam duration by the change of the concentration of electrolyte, while no such maximum is seen in the foaminess. The electrolyte concentration, at which the foam strength becomes maximum, and the coagulation value changes in the same trend from an electrolyte to the other. This is accounted for the fact that the affinity of polar part of dye ion to solvent is weakened by the addition of electrolyte.

Chemical Institute, Faculty of Science, the University of Tokyo, Tokyo.

(7) C. Robinson, *Proc. Roy. Soc.* (*London*), **A148**, 681 (1935); *Trans. Faraday Soc.*, **31**, 277 (1935).
(8) E. Valkó, *Trans. Faraday Soc.*, **31**, 231, 278, (1935).
(9) S. M. Neale, *Trans. Faraday Soc.*, **31**, 282 (1935).
(10) M. Nakagaki, This Bulletin, **22**, 200 (1949).

The Chlorination of Ethylene in Alcohol

By Kazuo SATAKE and Takeo KANEKO

(Received December 12, 1949)

It is well known that the chlorination of ethylene in aqueous solution yields ethylene chlorohydrine and dichloride. About the reactions, there are number of investigations, especially about the factor which is likely to determine the ratio of two additions, between ethylene and hypochlorous acid on the one hand, and between ethylene and chlorine on

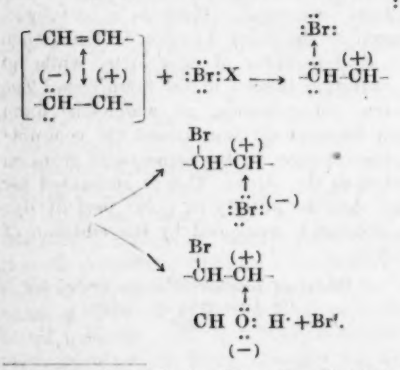
the other.[1][2][3]

$$H_2O+Cl_2 \rightleftarrows HOCl+H^++Cl^-$$
$$\downarrow CH_2=CH_2 \downarrow$$
$$ClCH_2CH_2Cl \qquad ClCH_2CH_2OH$$

Lately it was found that in other solvents as alcohol,[4][5][6][7] phenol[8] or organic acid,[9] the chlorination proceeded in a quite similar way and gave the substance which would be obtained by the addition of the alkyl, aryl or acyl hypochlorite corresponding to the reactive solvent, together with dichloride,

$$-CH=CH- + Cl_2 \xrightarrow{ROH} -CH(OR)CHCl- + -CHClCHCl-$$
$$\xrightarrow{RCOOH} -CH(OCOR)CHCl- + -CHClCHCl-,$$

and it was also found that the chlorine atom added to ethylenic linkage might be obtained from a compound in which chlorine atom was linked to oxygen,[4][5] nitrogen,[8] or a very negative organic radical as chloronitroform $ClC(NO_2)_3$,[10] instead of molecular chlorine. Recently Bartlett and Tarbell[7] stated that the reaction of this type might proceed as follows: one unsaturated carbon atom of the olefine donated a pair of electrons to bind the electrophylic halogen atom of the halogenating agent, while the nucleophillic addendum, either an anion or a negative fragment taken from a neutral solvent molecule, supplied a pair of electrons to form a linkage with other unsaturated carbon atom, *e. g.*,



So the reaction might be trimolecular, instead of dimolecular between olefine and hypochlorous acid or its derivatives. But the ratio of two products, chlorohydrine or its derivative and dichloride, seems to vary according to the kinds of the reactive solvent,[5][8][9] ethylenic linkage,[6] or chlorinating agent.[5] And the reaction condition itself, which was likely to influence the ratio of two products, has been less investigated, so the more detailed study of the chlorination of ethylene in alcohol is intended by the present authors to make clear the mechanism on the one hand, and to use the reaction for the preparation of chlorohydrine ether on the other. As the chlorinating agent, molecular chlorine was used.

From −40° to 10° the chlorination of ethylene proceeded rapidly and gave ethylene chlorohydrine ethyl ether and ethylene dichloride almost quantitatively. In this range of temperature, the higher the temperature, the greater the velocity was, but the ratio of both products scarcely changed, indicating that the temperature affected both additions in the same degree. Above 10°, acetaldehyde was produced as the result of the oxidation of alcohol by chlorine and the higher the temperature, the more the amount and the less the ratio of the ether in the reaction products was. When methyl alcohol was used as solvent, no oxidation was observed even at 20°. (Table 1.) However, the

Table 1
The Effect of Temperature

Temp., °C.	Yield of dichloride, %	Yield of chloroether, %	Acetaldehyde
−40	33	54	none
−10	34	56	〃
− 5	30	53	〃
0	33	51	〃
5	31	54	〃
10	32	50	trace
20	32	45	some
30	36	26	much

Ethyl alcohol 4.0 mol, chlorine 1.0 mol, ethylene 2.0 mol.

fractional distillation of the reaction products was more defficult than the case of ethyl alcohol, owing to the little difference of their boiling points. (Dichloride 84°, chlorohydrine methyl ether 92°)

Many catalysts of halogen-addition or -substitution (nucleophilic), as chloride of Hg, Al or Fe, were found to accelerate the both in the same degree, unless these substances did not markedly change the concentration of chloride ion in the reaction mixture. Active carbon, which adsorbed ethylene and chlorine on the porous surface, accelerated both additions, too. Such catalyst could not be found as to accelerate selectively only one of both additions, except urea, in the presence of which the ratio of the chloroether-formation seemed to increase somewhat.

(1) Gomberg, *J. Am. Chem. Soc.*, **41**, 1414 (1919).
(2) Ueno and Takase, *J. Soc. Chem. Ind., Japan*, **41**, 254 (1938).
(3) Hiratsuka, *J. Chem. Soc. Japan*, **58**, 1177 1937).
(4) Conat and Jackson, *J. Am. Chem. Soc.*, **46**, 1727 (1924); **48**, 2166 (1926).
(5) Likosherstov and Petrov, *J. Gen. Chem., U. S. S. R.*, **5**, 1348 (1935); *C. A.*, **30**, 2174 (1936).
(6) Meinell, *Ann.*, **510**, 129 (1934); **516**, 273 (1936).
(7) Bartlett and Tarbell, *J. Am. Chem. Soc.*, **58**, 466 (1936).
(8) Likosherstov and Arkhangel'skaya, *J. Gen. Chem., U.S.S.R.*, **7**, 1914 (1937); *C. A.*, **32**, 519 (1938).
(9) Weber, Hennion and Vogt, *J. Am. Chem. Soc.*, **61**, 457 (1939).
(10) Schmidt, Ascherl and Kuilling, *Ber.*, **57**, 1876 (1926).

On the other hand, hydrogen chloride produced during the ethoxy-and chlorine-addition, inhibited this addition selectively and the more the reaction proceded, the greater the ratio of the dichloride-formation became. When the concentration of chloride ion in the solution reached to 1/2 *N*, the formation of chloroether decreased remarkably and scarcely stopped till it became 2 *N*. The ether was obtained as main product only in the case of large excess of alcohol. (See Table 2.)

Table 2

The Effect of the Ratio of Reactants

Ethanol, mol	Chlorine, mol	Chlorine, ml./min.	Ethylene, mol	Ethylene, ml./min.	Yield of dichloride, %	Yield of chloroether, %	Final concn. of Cl
3.0	2.5	85	5.5	185	58	28	2.3
4.0	2.0	90	4.0	180	44	40	1.8
5.0	1.8	95	3.8	200	37	46	1.6
7.5	2.5	95	5.0	150	34	49	1.4
4.0	1.2	85	2.2	155	35	50	1.3
4.0	1.0	—	1.7	—	29	53	1.2
8.0	1.0	—	2.1	—	25	59	1.0
2.0	2.0	80	—	—	73	12	2.5
10.0	0.5	—	1.0	170	8	76	0.8

At 10°, yields were based upon the amount of chlorine introduced.

When the sufficient amounts of hydrogen or ammonium chloride were added to the solution at the beginning of the chlorination, no chlorohydrine ether was formed, though chlorine and ethylene reacted rapidly, giving ethylene dichloride as the sole product. While the presence of a considerable amount of sulfuric acid showed no effect to the ratio of both additions, though some polymerisation of ethylene occured by the acid. Acetic acid was the same, except that some other products (probably ethylene chlorohydrine acetate) were formed. So this apparent inhibition of ethoxy- and chlorine-addition was mainly due to chloride ion in the solution, and the effect of hydrogen ion was not so great.

In the presence of suitable chloride ion-combining substances such as Ag^+ or Pb^{++}, the ratio of chlorohydrine ether in the reaction mixtures increased greatly. Alkaline, which neutralized the hodrogen ion produced during the reaction, did not increase the chlorohydrine ether formation, but inhibited both additions at various degrees, as long as the concentration of chloride ion did not change by the effect of the cation. In these cases, the accumulation of insoluble chloride or the presence of insoluble neutralizating agent as ferric hydroxide seemed to affect adversely for the dissolving of the reacting gases into the solution. The adversed effects followed in the order : $Fe(OH)_3 \gg KCl$, $NaCl > NH_4Cl$, $Ca(OH)_2$

Table 3

The Effect of Many Substances

Addition of	Yield of dichloride, %	Yield of chloroether, %	Remarks
2*N*-HCl	96	0	Addition-velocity increased.
N/2-HCl	88	6	〃
N/2-NH_4Cl	78	11	
Ammonia* (a)	0	48	
〃 (b)	14	40	
〃 (c)	30	54	
NaOH(equiv. to Cl)	2	25	Large amount of acetaldehyde was formed.
$Ca(OH)_2$(〃)	26	45	
$Fe(OH)_3$(〃)	0	18	Ethylene was scarcely adsorbed.
ZnO (〃)	25	59	$ZnCl_2$ produced, catalyzed.
MgO (〃)	27	53	
PbO (〃)	10	68	
	8	74	
$AgNO_3$ (〃)	0	50	A nitro-ester was formed?
$Pb(NO_3)_2$(〃)	6	62	
$Pb(CH_3COO)_2$(〃)	17	56	An acetate was formed.
30% Water	31	25	Large amount of ethylene chlorohydrine and $\beta\beta'$-dichloroethyl ether were produced.
Active carbon 1 g.	41	57	Adsorption of ethylene was very rapid.
$HgCl_2$ 1 g.	39	54	The velocity of additions increased.
$AlCl_3$ 1 g.	38	53	〃
$FeCl_3$ 1 g.	40	52	〃
Urea 1 g.	30	57	〃
5 g.	31	65	〃
10 g.	27	68	〃
30 g.	18	69	〃
N-Acetic acid	35	50	Other chloro-compounds were formed.
N-Sulfuric acid	33	43	Some coloration occurred, with polymerisation of ethylene.

At 10°, ethyl alcohol 4.0 moles, chlorine 1.0 mole, ethylene 1.5 to 2.0 moles. The yield was based on the amount of chlorine introduced. * Ammonia was continuously introduced as gas; (a) large excess, (b) to maintain neutral, (c) slight acidic. The others were added at the beginning of the reaction.

$\gg$ PbO, $AgNO_3$, $PbCl_2$, AgCl. Those of the last four were very weak, so in the presence of oxide, nitrate, or acetate of Ag or Pb, ethylene chlorohydrine ether could be obtained in excellent yield.

In addition, the formation of small amounts of $\beta\beta'$-dichloro-diethylether was found, which increased with increment of water contents in the ethanol solution and of the reaction time. So it seemed to be produced according to the following reactions These results were summarized in Table 3.

$$CH_2 = CH_2 + H_2O + Cl_2 \longrightarrow ClCH_2CH_2OH$$

$$CH_2 = CH_2 + ClCH_2CH_2OH + Cl_2 \longrightarrow ClCH_2CH_2OCH_2CH_2Cl$$

Disscussion

It was supposed that ethyl hypochlorite was the intermediate of chloroether and the reaction proceeded as follows[6].

$$Cl_2 + C_2H_5OH \rightleftarrows C_2H_5OCl + H^+ + Cl'$$

$$CH_2 = CH_2 \swarrow \qquad \searrow \text{Decomposion}$$

$$ClCH_2CH_2Cl \quad C_2H_5OCH_2CH_2Cl \quad CH_3CHO + H^+ + Cl'$$

The facts that the greater acetaldehyde forms, the less chlorohydrine ether, but the amount of dichloride produced, remains constant, might support this assumption. Recently, similar addition of bromine to stilbene in methanol was examined by Bartlett and Tarbell.[7] According to them, the relative amounts of the dibromide and methoxy bromide in the reaction products varied with varing concentration of bromide ion in a way that it was consistent with the assumption that the positively charged intermediate might react in the following two ways.

$$C_6H_5CH = CHC_6H_5 + Br_2 \rightarrow C_6H_5\overset{(+)}{C}H - CHC_6H_5 + Br'$$

$$Br'(k_a) \swarrow \qquad \downarrow Br \qquad \downarrow CH_3OH(k_b)$$

$$C_6H_5CHBrCHBrC_6H_5 \quad C_6H_5CHBrCH(OCH_3)C_6H_5$$

So the relative amount of methoxybromide was equal to $k_b/[k_b + k_a(Br')]$, where (Br') represented the concentration of bromide ion and k the reaction constant of the above reaction. And the possibility that the bromohydrine ether might result from the direct additon of methyl hypobromite seemed to be disposed of kinetics, the rate being first order in stilbene and indepenedent of the acidity of the solution.

Our results that halide type catalysts accelerate both additions,[11] and that chloride ion inhibits the chloroether-formation selectively, and that the effect of hydrogen ion to the ratio of both reaction products is not so great, seem not only to be inconsistent with their assumption, but also even to verify it. But their equation does not agree with our results. It might be partially due to the other factor such as solubility- or activity-change of ethylene in the salt solution[3] or the difference of the dissociation coefficient of various chlorides (NH_4Cl, NaCl or HCl in alcohol). But the fact that the effect of chloride ion concentration to the chloroether-formation showed no simple relation as the bromination of stilben, might indicate that the solvolytic reaction proceeded by the more complex passes.

Urea seems to affect the reaction as halogenating catalyst[12] in the one hand, and as chloride ion-combining substance in the other.

Experimental Part

Ethylene.—The unsaturated hydrocarbon was prepared from ethyl alcohol by the use of acid clay (Takeda Pure Chemicals, Ltd.) as catalyst in quartz tube at 450° to 500°.[13] The issuing gases were passed through a water-cooling condenser, receiver of the condensate, two washing bottles containing water and then one containing concentrated sulfuric acid. Its purity was more than 98 per cent, freed from higher olefines.

Chlorine was produced from concentrated hydrochloric acid and potassium bichromate and washed with water in ordinary way. Its purity was more than 99 per cent.

Procedure.—200 to 1000 ml. of ethyl alcohol (96 per cent) was placed in a cylindrical bottle (diameter, 7.5 cm.), which was provided with 2 gas inlet tubes at the bottom and a tightly fitting stopper having 3 holes. The one was for an efficient sealed stirrer, the second carried a tube for connection with a trap cooled below $-10°$, and the third carried a thermometer. Ethylene and chlorine were introduced into alcohol through a flowmeter from the two gas inlet tubes at the bottom of the vessel, and the former was kept enough in excess over the latter to keep the reaction solution colorless, while the temperature of the solution controlled in the range of $\pm 3°$ by the suitable cooling and efficient stirring. Chlorine was adsorbed very rapidly and the issuing gas from the trap contained only ethylene in this condition.

After the definite amounts of chlorine was introduced, the mixture was added with the three times of water and the separated lower oil layer was washed with concentrated calcium chloride, sodium carbonate solution and water respectively and then dried with calcium chloride overnight. The upper aqueous layer was distilled and the fraction below 75° was added with the three times of water. Small amount of the separated oil was treated same as the oily layer above described. Then combined dried oil was distilled by fractionating column.

Ethylene dichloride..... b. p. 84°–85°, d (15°) 1.261. Cl % found: 68.21, 69.07. Calculated: 70.70.

Ethylen chlorohydrine ethylether.....b. p. 105°–107.5°, d (15°) 1.040, n (D, 20°) 1.418. Cl % found:

(11) It is posturated that the catalyst of this type accelerates the formation of the positively charged intermediate.

(12) Li, *J. Am. Chem. Soc.*, **69**, 1065 (1945).

(13) Katsuno, *J. Soc. Chem. Ind., Japan*, **42**, 908 (1939).

34.02, 33.84. Calculated: 32.65.

The distillation residue was dissolved in ether, and the ether solution was washed with solution of sodium carbonate and water, then dried with calcium chloride. After the removal of the solvent by distillation on a water-bath, the remaining oil was redistilled.

$\beta\beta'$-Dichloro-diethylether ..... b. p. 170°–173° (uncorr.) d (15°) 1.228, n (D, 20°) 1.457. Cl % found: 46.52, 47.36. Calculated: 48.86.

The approximate estimation of the ratio of dichloride and chloroether in the reaction mixtures could be done by the difference of the specific gravities between the two, if the amount of dichloroether was less than few per cent.

When the chlorination was done above 10°, some amounts of acetaldehyde was detected in the trap and the fore-run fraction (below 40°) of the upper aqueous layer. It was identified as p-nitro-phenylhydrazone (m. p. 128°), dimedone derivative (m. p. 139°–140°) and semicarbazone (m. p. 163°).

A number of substance shown in Table 3, except ammonia, were divided into very fine powder and added to alcohol in some portion during the introduction of gases. Ammonia was added through a flowmeter from the gas inlet tube with ethylene.

Properties of chlorohydrine ether as synthetic material or solvent are now on study.

In conclusion, the authors wish to express their thanks to Prof. Shiro Akabori, who gave many valuable advices and encouragements.

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1,2-Bis-(*p*-hydroxyphenyl)-1,2-dialkoxy-ethanes, Estrogenic Oxygen Analogs of Hexestrol[1]

By Yoshiyuki URUSHIBARA and Takeyoshi TAKAHASHI

(Received December 12, 1949)

E. C. Dodds, L. Goldberg, W. Lawson, and R. Robinson[2] pointed out a close structural resemblance of diethyl-stilbestrol, HOC_6H_4-$C(C_2H_5)=C(C_2H_5)C_6H_4OH$, just then prepared by them, to estrone or estradiol. Hexestrol, $HOC_6H_4CH(C_2H_5)CH(C_2H_5)C_6H_4OH$, another strong synthetic estrogen, is expected to bear a much closer structural resemblance to the natural estrogens, because it is a meso-form and the groups around carbon atoms 8 and 9 of the natural estrogens are arranged also in a "meso-form". This has been demonstrated by X-ray investigations.[3] The stereoisomerides, *d*-, *l*-, and racemic forms, of hexestrol have been reported to possess very weak potencies.[3]

The structural resemblance causing the development of similar physiological properties may be given by the union of two principal features, namely, a resemblance in the shapes of the molecular skeletons and the presence of the same functional groups at the corresponding positions of the similar-shaped skeletons. As for the skeleton, the replacement of the members constituting it with different atoms or groups may cause no radical change in the physiological action, unless the shape is altered significantly and unless an appearance of a new physiological action is associated with the replacement. Thus, the authors are interested in possible estrogenic activity of hexestrol analogs in which oxygen atom or the imino-group replaces one or both of the methylene groups or nitrogen atom one or both of the central methine groups.

One of such compounds is 1,2-bis-(*p*-hydroxyphenyl)-1,2-dimethoxy-ethane, HOC_6H_4-$CH(OCH_3)CH(OCH_3)C_6H_4OH$. It was already prepared by Th. Zincke and S. Münch.[4] They described a higher and a lower melting stereoisomerides without determining their configurations. The present authors presumed the higher melting compound to be the meso-form, and prepared it by the following improved method:

Bromine was added to diacetoxy-stilbene, $CH_3COOC_6H_4CH=CHC_6H_4OCOCH_3$, obtained by the acetylation of dihydroxy-stilbene, HO-$C_6H_4CH=CHC_6H_4OH$, and the resulting dibromide, $CH_3COOC_6H_4CHBrCHBrC_6H_4OCOCH_3$, was treated with an excess of sodium methoxide in methanol at room temperature. After left to stand overnight, the reaction mixture was poured into water, and acidified with hydrochloric acid. The precipitated substance was recrystallized from dilute methanol. The product thus obtained showed the melting point 220–222°, while Zincke and Münch gave 219–221°.

The minimum dose to produce typical oestrus in ovariectomized mice by subcutaneous injections in two portions in oil solution was found 0.5 gamma, and showed 5 percent activity of hexestrol evaluated by the same method.

(1) Preliminary note was published in the *Chemistry and Chemical Industry* (*Kagaku to Kogyo*), **2**, No. 2, 34 (1949).

(2) *Nature*, **141**, 247 (1938).

(3) C. H. Carlisle and D. Crowfoot, *J. Chem. Soc.*, **1941**, 6; also cf. U. v. Solmssen, *Chem. Rev.*, **37**, 481 (1945).

(4) *Ann.*, **335**, 157 (1904).

Considering that the simple dihydroxy-dibenzyl, $HOC_6H_4CH_2CH_2C_6H_4OH$, shows only a very weak activity, the minimum active dose being as much as 100 mg. in rats, the two methoxy groups proved really quite effective in imitating the molecular shape of hexestrol, and thus it has been indicated that the methylene groups in the ethyl groups of hexestrol can be replaced with oxygen atoms without causing any fundamental change in the physiological properties. Further, the strong activity has demonstrated that the configuration of the compound used is in fact a meso-form.

The corresponding diethoxy-compound, 1,2-bis-(*p*-hydroxyphenyl)-1,2-diethoxy-ethane, $HOC_6H_4CH(OC_2H_5)CH(OC_2H_5)C_6H_4OH$, was newly synthesized by a similar method using sodium ethoxide in ethanol instead of sodium methoxide in methanol. It forms colorless needles when recrystallized from dilute ethanol, melts at 212.5–214.5°, and shows similar solubilities in various solvents to the methoxy-compound. As expected, it showed a far smaller potency than the methoxy-compound, the minimum active dose being 10 gammas.

A nitrogen analog of hexestrol dimethyl ether, ethyl-*p*-methoxyphenyl-(1-*p*-methoxyphenyl-propyl)-amine, $CH_3OC_6H_4N(C_2H_5)CH(C_2H_5)C_6H_4OCH_3$, m.p. 63.5°, has been prepared. It developed incomplete but distinct durable oestrus. A more detailed account will soon appear.[5] In this connection, it may be added that J. B. Niederl and M. I. Dexter[6] have found blood-pressure lowering, but no oestrus producing, action in 1,2-bis-(*p*-hydroxyphenyl)-1,2-di-(methylamino)-ethane, $HOC_6H_4CH(NHCH_3)CH(NHCH_3)C_6H_4OH$. In the present authors' opinion, however, it must be determined whether the compound is really a meso-form or not before concluding estrogenic inactivity of the nitrogen analog of hexestrol represented by the above formula.

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(5) A preliminary note was presented by Y. Nomura at the annual meeting of the Chemical Society of Japan on April 3, 1949.

(6) *J. Am. Chem. Soc.*, **70**, 3071 (1948).

Calculations of the Energy Levels of Cycloöctatetraene (C_8H_8)

Ikuzo TANAKA and Shoji SHIDA

(Received October 21, 1949)

1. Introduction

The cycloöctatetraene molecule has already been treated by Hückel[1] according to the molecular orbital method. But as its molecular structure was not known at the time, he treated its molecule as plane and suggested the possibility of its substance to be paramagnetic.

Lately, by R. C. Pink and A. R. Ubbelohde[2] and also by the members of our laboratory[3] it is found experimentally that the substance is not paramagnetic but diamagnetic* like many other organic substances and also that its molecule has no resultant spin in the ground state. The purpose of the present paper is to calculate the energy levels of the molecule from the stand-point of the Heitler-London-Slater-Pauling method,[4][5][6] assuming different structures (D_{2d} and D_{4d}) proposed by different investigators and from different experimental grounds, and also to show which structure is in better agreement with the experimental results of magnetic susceptibility, absorption spectra and thermochemical data.

The structure of cycloöctatetraene, though investigated by several physico-chemical methods, but has not yet been decided. Until now, as a result of investigation, the structures of C_8H_8, "Crown Form"[7][8][9] (D_4, or D_{4d}) and "Tub Form" (D_{2d})[10][11][12] are reported. (Fig. 1).

* The molar magnetic susceptibility was found in our laboratory to be -55.3×10^{-6}, independent of the temperature between 20° and 80°.

(1) E. Hückel, *Z. Physik*, **70**, 204 (1931).

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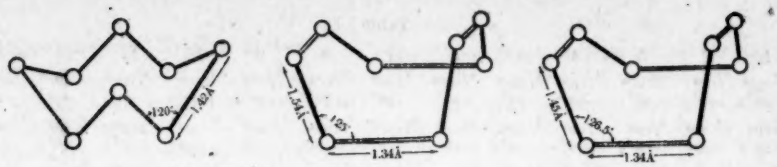

D_{4d} (Gas phase by the method of electron diffraction[7])

D_{2d} (Solid phase by the method of X-ray diffraction[10][11])

D_{2d} (Gas phase by the method of electron diffraction[12])

Fig. 1.

First, in calculating the energy levels of C_8H_8 as the symmetry of D_{2d}, a molecule of C_8H_8 is treated as follows: Each carbon atom has one π-electron whose density cloud is a dumbbell with its axis perpendicular to the plane of the σ-bonds (approximately sp^2-bonds). It is assumed that the interaction of the π-electron and the σ-electron is small.

2. Calculation of Singlet States

All the possible structures will be described first. They are linearly independent, namely, the canonical sets for cyclooctatetraene; the two Kekule structures (Ψ^1, Ψ^2), the eight Dewar I structures (Ψ^3, Ψ^5, ..., Ψ^{10}) and the four Dewar II structures (Ψ^{11}, Ψ^{12}, Ψ^{13}, Ψ^{14}) exist. These are shown in Fig. 2. For instance, two Kekule structures for benzene have identical energy, but those for cyclooctatetraene (D_{2d}) have not. This arises from the fact that the exchange integral is devided into two.

$\Psi^k (k=1, 2, 3, \ldots, 14)$, wave function attached to the each structure k of the canonical set, is

$$\Psi^k = \frac{1}{2^4(8!)^{\frac{1}{2}}} \sum_p (-1)^p P \psi_1(1)\psi_2(2)(\alpha_1\beta_2-\beta_1\alpha_2) \times \psi_3(3)\psi_4(4)(\alpha_3\beta_4-\beta_3\alpha_4)\times \quad \ldots.(1)$$

The energy levels are given by solving the secular equation

$$\det \| \Psi^j \mid H-W \mid \Psi^k \| = 0 \quad \ldots.(2)$$

$$(\Psi^j \mid H-W \mid \Psi^k) = U_{jk}(Q-W)+V_{jk}\alpha+W_{jk}\alpha' \quad \ldots.(3)$$

$$Q = \int \psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4)\psi_5(5)\psi_6(6)\psi_7(7) \psi_8(8) H \tilde{\psi}_1(1)\tilde{\psi}_2(2)\tilde{\psi}_3(3)\tilde{\psi}_4(4)\tilde{\psi}_5(5)\tilde{\psi}_6(6) \tilde{\psi}_7(7)\tilde{\psi}_8(8)d\tau \quad \ldots.(4)$$

$$\alpha = \int \psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4)\psi_5(5)\psi_6(6)\psi_7(7) \cdot \psi_8(8) H \tilde{\psi}_1(2)\tilde{\psi}_2(1)\tilde{\psi}_3(3)\tilde{\psi}_4(4)\tilde{\psi}_5(5)\tilde{\psi}_6(6) \tilde{\psi}_7(7)\tilde{\psi}_8(8)d\tau \quad \ldots.(5)$$

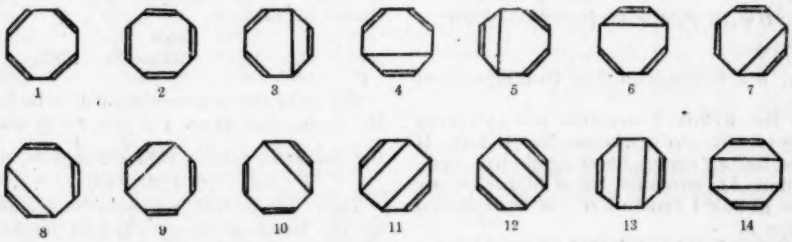

Fig. 2.—1~2, Kekule structures; 3~10, Dewar I structures; 11~14, Dewar II structures.

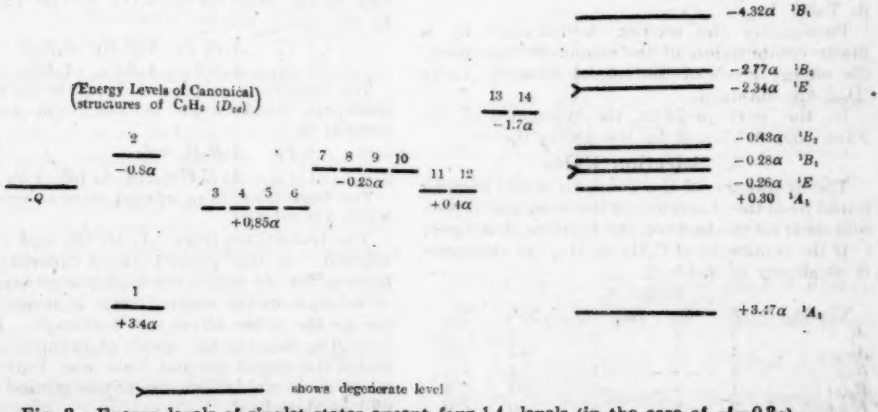

Fig. 3.—Energy levels of singlet states except four $^1A_1$ levels (in the case of $\alpha'=0.3\alpha$).

Table 1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	$^{8}/_{32}\alpha$ $-16\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{16}\alpha$ $-2\alpha'$	$^{4}/_{16}\alpha$ $-2\alpha'$	$^{4}/_{16}\alpha$ $-2\alpha'$	$^{4}/_{16}\alpha$ $-2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{4}/_{16}\alpha$ $-8\alpha'$	$^{4}/_{16}\alpha$ $-8\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$
2	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{8}/_{32}\alpha'$ -16α	$^{2}/_{2}\alpha$ $+8\alpha'$	$^{2}/_{2}\alpha$ $+8\alpha'$	$^{2}/_{2}\alpha$ $+8\alpha'$	$^{2}/_{2}\alpha$ $+8\alpha'$	$^{4}/_{16}\alpha'$ -2α	$^{4}/_{16}\alpha'$ -2α	$^{4}/_{16}\alpha'$ -2α	$^{4}/_{16}\alpha'$ -2α	$^{2}/_{2}\alpha$ $+8\alpha'$	$^{2}/_{2}\alpha$ $+8\alpha'$	$^{4}/_{16}\alpha'$ -8α	$^{4}/_{16}\alpha'$ -8α
3	$^{4}/_{16}\alpha$ $-2\alpha'$	$^{2}/_{2}\alpha$ $+8\alpha'$	$^{8}/_{8}\alpha$ $-1\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$
4	$^{4}/_{16}\alpha$ $-2\alpha'$	$^{2}/_{2}\alpha$ $+8\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{8}/_{8}\alpha$ $-1\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$
5	$^{4}/_{16}\alpha$ $-2\alpha'$	$^{2}/_{2}\alpha$ $+8\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{8}/_{8}\alpha$ $-1\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$
6	$^{4}/_{16}\alpha$ $-2\alpha'$	$^{2}/_{2}\alpha$ $+8\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{8}/_{8}\alpha$ $-1\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$
7	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{4}/_{16}\alpha'$ -2α	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{8}/_{8}\alpha'$ -1α	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{2}/_{8}\alpha'$ $+2\alpha$
8	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{4}/_{16}\alpha'$ -2α	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{8}/_{8}\alpha'$ -1α	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{2}/_{8}\alpha'$ $+2\alpha$
9	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{4}/_{16}\alpha'$ -2α	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{8}/_{8}\alpha'$ -1α	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{2}/_{8}\alpha'$ $+2\alpha$
10	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{4}/_{16}\alpha'$ -2α	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{8}/_{8}\alpha'$ -1α	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{2}/_{8}\alpha'$ $+2\alpha$
11	$^{4}/_{16}\alpha$ $-8\alpha'$	$^{2}/_{2}\alpha$ $+8\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{8}/_{8}\alpha$ $-16\alpha'$	$^{2}/_{8}\alpha$ $-4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$
12	$^{4}/_{16}\alpha$ $-8\alpha'$	$^{2}/_{2}\alpha$ $+8\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{2}/_{8}\alpha$ $-4\alpha'$	$^{8}/_{8}\alpha$ $-16\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$
13	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{4}/_{16}\alpha'$ -8α	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{8}/_{8}\alpha'$ -16α	$^{2}/_{8}\alpha'$ -4α
14	$^{2}/_{8}\alpha$ $+2\alpha'$	$^{4}/_{16}\alpha'$ -8α	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{4}/_{4}\alpha$ $+4\alpha'$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{2}/_{8}\alpha'$ $+2\alpha$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{1}/_{4}\alpha$ $+4\alpha'$	$^{2}/_{8}\alpha'$ -4α	$^{8}/_{8}\alpha'$ -16α

Notation $^{8}/_{32}\alpha-16\alpha' = 8(Q-W)+(32\alpha-16\alpha')$

$$\alpha' = \int \psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4)\psi_5(5)\psi_6(6)\psi_7(7)\psi_8(8) H \tilde{\psi}_1(1)\tilde{\psi}_2(3)\tilde{\psi}_3(2)\tilde{\psi}_4(4)\tilde{\psi}_5(5)\tilde{\psi}_6(6)\tilde{\psi}_7(7)\tilde{\psi}_8(8) \quad \ldots.(6)$$

U_{jk}, V_{jk}, W_{jk} is determined by Pauling's island method.

Then the Kekule I structure has an energy lowering of $(4\alpha-2\alpha')$, whereas the Kekule II structure has an energy lowering of $(4\alpha'-2\alpha)$. The Kekule II structure has a higher energy than the Kekule I structure $\alpha'<\alpha$ as explained in Section 5.

The determinant evaluated for cyloöctatetraene (fourteen canonical structures) is shown in Table 1.

Factorizing the secular determinant by a linear combination of the canonical structures, the energy levels of the singlet states of C_8H_8 (D_{2d}) are obtained.

In the next problem, the symmetry of the levels may be found by the group theory.

3. Selection Rules

The symmetry of the fourteen levels may be found from the characters of the reducible representation on the basis of the fourteen structures.

If the symmetry of C_8H_8 is D_{2d}, its character is as shown in Table 2.

Table 2

$V_d=D_{2d}$	E	C_2	$2iC_4=2S_4$	$2C'_2$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
B_1	1	1	−1	1	−1
$B_2(z)$	1	1	−1	−1	1
$E(x\pm iy)$	2	−2	0	0	0

The characters of the symmetry operations in the reducible representation Γ for C_8H_8 are shown in Table 3.

Table 3

	E	C_2	$2iC_4=2S_4$	$2C'_2$	$2\sigma_d$
Γ	14	6	2	6	6

The reducible representation Γ is broken into its irreducible parts $\Gamma=\sum_j a_j\Gamma_j$ by means of the character tables (Tables 2 and 3), namely

$$\Gamma = 6A_1+2B_1+2B_2+2E \quad \ldots.(7)$$

These irreducible repesentations correspond to the fourteen energy levels of singlet state. The selection rule for transitions between $^1A_1$ and all the other energy levels will be discussed by the group theory.

$$\begin{cases} P_z & A_1B_2A_1,\ A_1B_2B_1,\ A_1B_2E \\ P_x, P_y & A_1EA_1,\ A_1EB_1,\ A_1EB_2 \end{cases}$$

The transitions from ground state to the excited levels are forbidden for reduced form does not contain A_1.

$$\begin{cases} P_z & A_1B_2B_2 = A_1 \\ P_x, P_y & A_1EE = A_1+A_2+B_1+B_2 \end{cases}$$

The transitions from ground state to the B_2, E levels are allowed.

The transitions from $^1A_1$ to $^1B_2$ and ^1E are allowed. In this point C_8H_8 is different from benzene for the transition from the ground state of benzene to the excited state is forbidden so far as the polar terms are neglected. In the following chapter the result of calculation, by which the singlet ground state was found out to be more stable than the triplet ground state, will be described.

4. Calculation of Triplet States

The triplet states of cyclooctatetraene are calculated by analogous method to that in the case of the singlet states.

The canonical set is composed of twenty eight structures. But the energy of triplet ground state is approximately the lowest of those, calculated from the only eight canonical structures in the case of D_{2d}, because the remaining twenty canonical structures have higher energies than the former.

The eight canonical structures are shown in Fig. 4 and the secular determinant is given in Table 4.

Table 5

The Energy Levels of Singlet States of C_8H_8 Except Four $^1A_1$ Levels.

	$\alpha'=0.2\alpha$	$\alpha'=0.25$	$\alpha'=0.3\alpha$	$\alpha'=0.35\alpha$
$^1B_1$	-4.21α	-4.27α	-4.32α	-4.38α
$^1B_2$	-2.48α	-2.62α	-2.77α	-2.92α
^1E	-2.22α	-2.28α	-2.34α	-2.41α
$^1B_2$	-0.32α	-0.38α	-0.43α	-0.48α
$^1B_1$	-0.19α	-0.23α	-0.28α	-0.32α
^1E	-0.18α	-0.22α	-0.26α	-0.29α
$^1A_1$	0.10α	0.20α	0.30α	0.40α
$^1A_1$	3.63α	3.55α	3.47α	3.40α

state.

In order to determine the value of the splitting up of the energy levels, it is necessary to find the numerical values of α, α'. The two

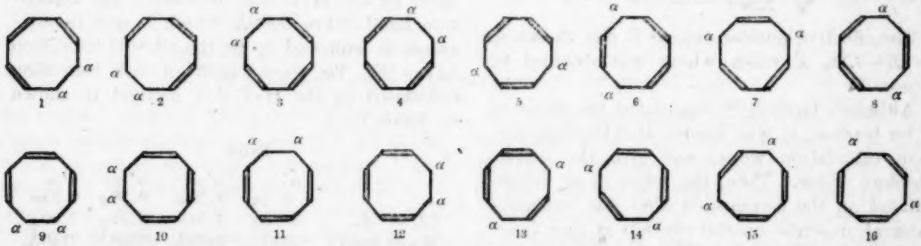

Fig. 4.—Upper eight canonical structures are used for the triplet states of D_{2d} and all of sixteen canonical structures for the triplet states of D_{4d}.

Table 4

	1	2	3	4	5	6	7	8
1	$8/16\alpha-16\alpha'$	$0/4\alpha'$	$0/0$	$0/4\alpha'$	$4/8\alpha-2\alpha'$	$0/2\alpha'$	$0/2\alpha'$	$4/8\alpha-2\alpha'$
2	$0/4\alpha'$	$8/16\alpha-16\alpha'$	$0/4\alpha'$	$0/0$	$4/8\alpha-2\alpha'$	$4/8\alpha-2\alpha'$	$0/2\alpha'$	$0/2\alpha'$
3	$0/0$	$0/4\alpha'$	$8/16\alpha-16\alpha'$	$0/4\alpha'$	$0/2\alpha'$	$4/8\alpha-2\alpha'$	$4/8\alpha-2\alpha'$	$0/2\alpha'$
4	$0/4\alpha'$	$0/0$	$0/4\alpha'$	$8/16\alpha-16\alpha'$	$0/2\alpha'$	$0/2\alpha'$	$4/8\alpha-2\alpha'$	$4/8\alpha-2\alpha'$
5	$4/8\alpha-2\alpha'$	$4/8\alpha-2\alpha'$	$0/2\alpha'$	$0/2\alpha'$	$8/8\alpha-4\alpha'$	$2/4\alpha+2\alpha'$	$0/2\alpha'$	$2/4\alpha+2\alpha'$
6	$0/2\alpha'$	$4/8\alpha-2\alpha'$	$4/8\alpha-2\alpha'$	$0/2\alpha'$	$2/4\alpha+2\alpha'$	$8/8\alpha-4\alpha'$	$2/4\alpha+2\alpha'$	$0/2\alpha'$
7	$0/2\alpha'$	$0/2\alpha'$	$4/8\alpha-2\alpha'$	$4/8\alpha-2\alpha'$	$0/2\alpha'$	$2/4\alpha+2\alpha'$	$8/8\alpha-4\alpha'$	$2/4\alpha+2\alpha'$
8	$4/8\alpha-2\alpha'$	$0/2\alpha'$	$0/2\alpha'$	$4/8\alpha-2\alpha'$	$2/4\alpha+2\alpha'$	$0/2\alpha'$	$2/4\alpha+2\alpha'$	$8/8\alpha-4\alpha'$

The secular determinant is factorized by linear combination of eight canonical structures like the singlet states. The same parameter, α, appeared as it did in the energy of the singlet states. The energy of the triplet ground state calculated is -1.84α (if $\alpha'=0.2\alpha$) or -1.76α (if $\alpha'=0.3\alpha$). Therefore, it is expected from the H-L-S-P method that C_8H_8 is diamagnetic.*

5. Energy Levels and Resonance Energy

The energy levels of singlet states of C_8H_8, except four $^1A_1$ levels in each case of $\alpha'=0.2\alpha$, 0.25α, 0.3α, 0.35α, are given in Table 5. The reason why the values of α' are selected as above will be shown in section 7

The two Kekule structures have not the same energy and the higher Kekule structure scarcely affects the ground state. Then the lower Kekule structure, the four lower Dewar I structures and the two lower Dewer II structures greatly contribute to the energy of the ground state.

* The results calculated by the G-M-S method also suggest us that $C_8H_8(D_{2d})$ is diamagnetic. This calculation will be publisded.

methods of finding these values are as follows: first, experimentally from thermochemical data, secondly, theoretically by the $2p\pi$ hydrogen-like functions.

The heat of formation is calculated from recent data.[13]

$$8C+8H=C_8H_8+1354.8 \text{ kcal.}$$

The values of bond energy obtained from recent data[14] are as follows:

C-C= 60.3 kcal.
C-C=102.9 kcal.
C-H= 87.15 kcal.
$\longrightarrow$ therefore the heat of formation of $C_8H_8=1350$ kcal.

This difference, 4.8 kcal, may be taken as the experimental resonance energy which is about 11%~13% of that for benzene. (Benzene, $\alpha=-1.55$[15] or -1.92 e.V.[16])

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(14) J. L. Cotrell and L. E. Sutton, *J. Chem. Phys.*, **15**, 685 (1947).
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(16) G. B. Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Am. Chem. Soc.*, **58**, 152 (1936).

But it is necessary to examine critically the resonance energy of this experimental data. The structure of C_8H_8 is not plane, therefore, the steric hindrance demands considerations. Namely, the steric influences between CH and CH, and that of the bond energy of C=C must be taken into considerations.

Next we shall calculate by the $2p\pi$ hydrogen-like functions. The structure of cyclooctatetraene proposed by Hedberg and Schomaker[12] is as follows:

$\angle CCC = 126.5°$ C=C=1.34 Å. C−C=1.45 Å.

The eigenfunctions are

$$\Psi_\pi(r,\theta,\varphi) = \sqrt{\frac{Z^5}{32\pi}} e^{-Zr/2} r \sin\theta\cos\varphi \quad (8)$$

The effective nuclear charge Z was chosen to be $Z=3.18$, a value which was obtained by Zener.[17]

Although Griffing[18] calculated the value of α for benzene, it was known that this approximate calculation would not give the correct absolute value. Then, the value of α' is calculated on the assumption that the exchange integral depends on the overlap of $2p\pi$ function, as this value depends on approximately the angle between $2p\pi$ functions at the neighboring carbon nuclei and $\alpha'=0.3\alpha$ is obtained. Then energy levels are calculated using various value of $\alpha'(0.20\alpha, 0.25\alpha, 0.30\alpha, 0.35\alpha)$. The resonance energy is calculated by use of $\alpha=1.5$ e.V. This value of α is obtained with regard to the exchange integral of benzene and the effect of geometrical form of cyclooctatetraene upon the strength of binding in comparison with that of benzene. But the exact value of α must be obtained in future from the detailed experimental data.

Table 6

	$\alpha'=0.2\alpha$	$\alpha'=0.25\alpha$	$\alpha'=0.30\alpha$	$\alpha'=0.35\alpha$
Ground state	3.63α	3.55α	3.47α	3.40α
Kekule I	3.60α	3.50α	3.40α	3.30α
Resonace energy	0.03α	0.05α	0.07α	0.10α
	1.04 kcal.	1.73 kcal.	2.42 kcal.	3.46 kcal.

The larger the exchange integral α', the larger the resonance energy grows, as mentioned above.

6. Absorption Spectrum

The absorption spectrum of cyclooctatetraene[19] is shown in Fig. 5.

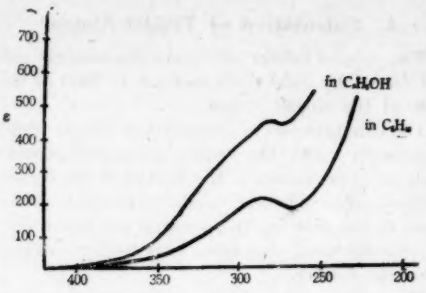

Fig. 5.

In our judgment about the value of ε, the shoulder of the absorption band 2800 Å. is the forbidden transition. Hence this absorption band may be the $^1A_1 \rightarrow {}^1A_1$ transition calculated by the H-L-S-P method.* The absorption band below 2000Å. which is now investigated, is supposed to be the allowed transition $^1A_1 \rightarrow {}^1E$. The wave lengths of each transition calculated by the H-L-S-P method is shown in Table 7.

Table 7

	$\alpha'=0.2\alpha$	$\alpha'=0.25\alpha$	$\alpha'=0.30\alpha$	$\alpha'=0.35\alpha$
$^1A_1 \rightarrow {}^1A_1$	3.53α	3.35α	3.17α	3.00α
Wave length	2330Å.	2460Å.	2600Å.	2740Å.
$^1A_1 \rightarrow {}^1E$	3.81α	3.77α	3.73α	3.69α
Wave length	2160Å.	2180Å.	2210Å.	2230Å.

7. In the Case of D_{4d}

The experimental results that the structure of cyclooctatetraene may be "Crown Form" (D_{4d}) are reported by O. Bastiaisen, O. Hassel and A. Langseth[7] (electron diffraction), and so the energy levels of C_8H_8 is calculated to have the symmetry of D_{4d} by the H-L-S-P method. The procedure of calculation is similar to that in the case of D_{2d}.

In the symmetry D_{2d} there are two different exchange integrals α and α', but in D_{4d} $\alpha=\alpha'$, so the energies of two Kekule structures are identical. Then the determinant of C_8H_8 (D_{4d}) is obtained by putting $\alpha=\alpha'$ in the determinant of D_{2d}. The energy levels of singlet states of C_8H_8 (D_{4d}) are obtained after calculating the above determinant, and the symmetry of the levels is decided from the group theory, and the transition only from $^1A_1$ to the symmetry $^1E_1$ is allowed. The results are shown in Fig. 9.

For the purpose of obtaining the energy of the triplet ground state the calculation is made using sixteen canonical structures, excepting

(17) C. Zener, *Phys. Rev.*, **36**, 51 (1930).
(18) V. Griffing, *J. Chem. Phys.*, **15**, 421 (1947).
(19) S. Miyakawa, unpublished.

* We obtain that $^1A_2$ level is lower than $^1A_1$ level calculating by the G-M-S method, and the calculation by the H-L-S-P method including polar terms produces $^1A_2$ level, where the value of $^1A_2$ level cannot be calculated because the new Coulomb integral and exchange integral are not known exactly. So we cannot decide whether 2800Å. band is the $^1A_1 \rightarrow {}^1A_1$ transition or the $^1A_1 \rightarrow {}^1A_2$ transition.

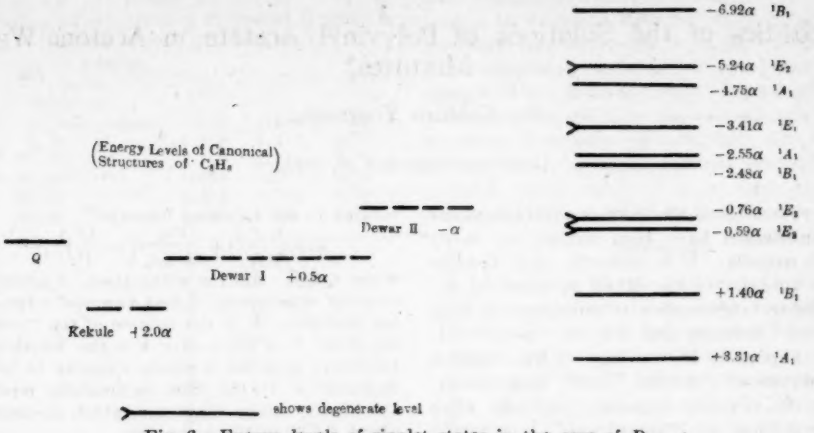

Fig. 6.—Energy levels of singlet states in the case of D_{4d}.

the twelve structures which have higher energies in twenty eight structures, and get 2.24α as the energy of the triplet ground state. The energy of the singlet ground state (3.31α) is lower than that of the triplet ground state (2.24α). The singlet state $^1A_1$ is, therefore, the ground state of cyclooctatetraene, and it is expected to be diamagnetic from the standpoint of the H-L-S-P method.

The resonance energy for C_8H_8 (D_{4d}) is as following. The singlet ground state ($^1A_1$) has the energy 3.31α, (Fig. 6) whereas one Kekule structure which is the structure of the lowest energy, has an energy of 2.0α. The difference, 1.31α, between the energy of the ground state and that of the Kekule structure is resonance energy.[20] The resonance energy for C_8H_8 is experimentally 4.8 kcal. (§ 5), then $1.31\alpha = 4.8$ kcal., and we obtain $\alpha = 3.66$ kcal. And, theoretically, the values of α in each case of various angles between carbons are calculated, on the assumption that the Hamiltonian of C_8H_8 is approximately the same as that C_6H_6 and the exchange integral depends on the overlap of $2p\pi$ function as this value depends on approximately the angle between $2p\pi$ functions at the neighboring carbon nuclei (Table 8). The value of α which is calculated from the absorption spectrum is different from that obtained from the thermochemical data and the numerical calculation. If the structure of cyclooctatetraene is D_{4d}, $\angle$CCC angle may be greater than 120°[8], because in case of 120° the resonance energy is so small that cyclooctatetraene cannot exist stable. $\angle$CCC of cyclooctatatetraene forms the angle that is unstabilized by the steric hindrance and stabilized by the resonance energy balance.

Table 8

$\angle$CCC	$2p\pi \sim 2p\pi$ angle	α e. V.	α kcal.
120°	80°	-5.31×10^{-2}	− 1.22
121°	78°	-7.61×10^{-2}	− 1.75
122°	75.8°	-1.06×10^{-1}	− 2.44
128°	73.4°	-1.45×10^{-1}	− 3.34
124°	71.5°	-1.77×10^{-1}	− 4.08
125°	68°	-2.48×10^{-1}	− 5.72
126°	65°	-3.17×10^{-1}	− 7.31
127°	61.2°	-3.68×10^{-1}	− 8.48
128°	58.3°	-4.89×10^{-1}	−11.27

(20) G. W. Wheland, *J. Chem. Phys.*, **2**, 474 (1934). Resonance Energy $= 1.29\alpha$.

So far the interaction only between neighboring atoms has been considered. But if cyclooctatetraene is D_{4d} and α is small, the interaction between the second neighboring atoms is not neglected. In respect to this point a further investigation is going on.

Summary

The energy levels of cyclooctatetraene as D_{2d} and D_{4d} were calculated by the H-L-S-P method. Then we showed that the ground state of C_8H_8 (D_{2d} and D_{4d}) may be diamagnetic. The resonance energy of C_8H_8 (D_{2d} and D_{4d}) is about several kilocalories (about ten per cent of that of benzene) from thermochemical data and numerical calculation. The wave length of absorption spectra calculated assuming D_{2d} is in better agreement with the experimental result than that calculated assuming D_{4d}.

The authors wish to express their appreciation to Professor Mikio Tamura at Kyoto University for some very helpful correspondence and discussion. The helpful suggestions of Kazuo Niira, Seikyo Mizushima and Saburo Nagakura are gratefully acknowledged.

Laboratory of Physical Chemistry, Tokyo Institute of Technology, Tokyo

Viscosities of the Solutions of Polyvinyl Acetate in Acetone-Water Mixtures*

By Koshiro YOSHIOKA

(Received December 26, 1949)

The viscosities of the solutions of high molecular substances have been studied by many authors recently. It is generally said that the specific viscosity of the dilute solutions of flexible linear macromolecular substance is high in "good" solvents and low in "poor" solvents. Especially in the case of the solution in a mixture of "solvent" and "nonsolvent," the specific viscosity decreases gradually when the proportion of "nonsolvent" increases.[1] There appears a maximum in the specific viscosity of the solutions of polyvinyl acetate in methanol-water mixtures, which has been observed by Matsumoto.[2] In the present report, the results of the viscosity measurements on the dilute solutions of polyvinyl acetate in acetone-water mixtures, will be described.

Experimental

Polyvinyl Acetate.—The sample of polyvinyl acetate made by Dai-Nippon Celluloid Company has been used in the experiments. Insoluble polymer was removed from the sample by dissolving it in acetone and filtering carefully. After filtration the polymer was precipitated from the acetone solution by pouring it slowly into water, and the precipitated polymer was dried in vacuum. The same stock sample was used throughout the experiment. The osmotic molecular weight of the present sample was determined to be 155,000 by Endo.[3]

Acetone.—Ordinary material was boiled with potassium permanganate for some hours and then distilled with the addition of potassium carbonate. The distillate was dehydrated over calcium chloride and fractionated.

Solutions.—Solutions were prepared by dissolving polyvinyl acetate in acetone-water mixtures of varying proportions. The composition of the solvent varied from pure acetone to 25 vol.-% of water. The concentration was determined by evaporating the solution to dryness and expressed in grams of polymer per 100 cc. of solution.

Viscosity Measurement.—Viscosities were measured at 20±0.02° in the ordinary manner, by means of an Ostwald type capillary viscometer. The relative viscosities (η_r) were calculated according to the following formula[4]

$$\eta_r = \frac{t}{t_0}\frac{d}{d_0}\left\{1+\frac{Vd_0}{8\pi l\eta_0 t_0}\left(1-\frac{t_0^2}{t^2}\right)\right\}, \qquad (1)$$

where t_0 and t are the efflux times of solvent and solution respectively; d_0 and d are the corresponding densities; V is the volume of the "measuring bulb" in a viscometer; l is the length of the capillary; η_0 is the absolute viscosity of solvent. In equation (1), the term in brackets represents the kinetic energy correction, which amounted to about 1·3 % in the worst case.

Results and Discussion

The resulting data are plotted in Fig. 1 as the specific viscosity ($\eta_{sp}=\eta_r-1$)-concentration (c) ratio against the concentration, with varying proportions of water. As is clear from Fig. 1, the concentration dependence of specific viscosity is well expressed by the following equation in low concentration range

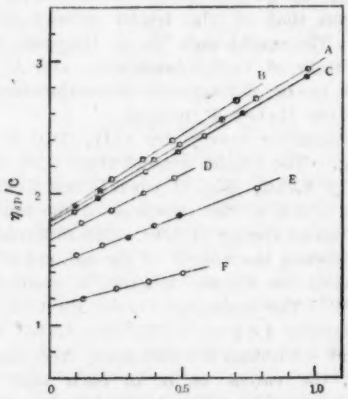

Fig. 1.—Specific viscosities of solutions of polyvinyl acetate in acetone-water mixtures at 20°. (A) Pure acetone; (B) Water 4.76%; (C) Water 10%; (D) Water 15.38%; (E) Water 20%; (F) Water 25%.

$$\eta_{sp}/c=[\eta]+Kc, \qquad (2)$$

where $[\eta]$ and K are constants. $[\eta]$ is the limiting value of η_{sp}/c at infinite dilution and usually called intrinsic viscosity. Equation (2) may also be expressed as follows

$$\eta_{sp}/c=[\eta]+k[\eta]^2c, \qquad (3)$$

where $k=K/[\eta]^2$ and is a dimensionless number.

$[\eta]$ and K are calculated by the method of least squares and given as function of solvent composition in Table 1, Fig. 2 and Fig. 3. In Table 1 is also given the value of k.

* Read before the annual meeting of the Society on April 1, 1949.

(1) T. Alfrey, A. Bartovics and H. Mark, *J. Am. Chem. Soc.*, **64**, 1557, (1942); T. Alfrey, *J. Colloid Sci.*, **2**, 99, (1947).

(2) S. Matsumoto, *The Chemistry of High Polymer* (*Kobunshi Kagaku*), **6**, 179, (1949).

(3) K. Endo, *J. Chem. Soc., Japan*, **71**, 232, (1950).

(4) R. H. Wagner, *Anal. Chem.*, **20**, 155, (1948).

Table 1

Viscosities of Solutions of Polyvinyl Acetate in Acetone-Water Mixtures at 20°

Compn. of solvent (Vol. % of water)	$[\eta]$	K	k
0 (pure acetone)	1.785	1.184	0.37
4.76	1.800	1.273	0.39
10.00	1.746	1.171	0.38
15.38	1.654	0.967	0.35
20.00	1.454	0.746	0.35
25.00	1.140	0.505	0.39

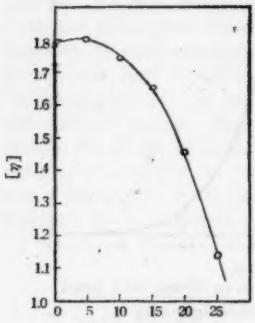

Fig. 2.—Effect of solvent composition on $[\eta]$.

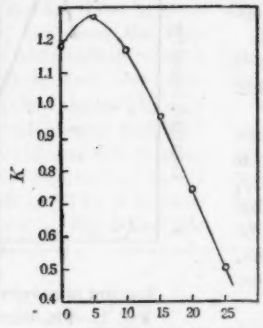

Fig. 3.—Effect of solvent composition on K.

For solvents containing up to about 10% water, the change of the intrinsic viscosity is small, and even a slight maximum is observed. From this experimental fact, it is supposed that the extension of polyvinyl acetate molecule in acetone is not appreciably changed by the addition of a small amount of water, in spite of its nature as typical nonsolvent. A similar result was obtained by Endo[3] from his osmotic measurements on the same system.

With a larger content of water, the intrinsic viscosity decreases as usual.

It is to be noted that k does not vary appreciably (i.e. $0.35 \sim 0.39$) as the amount of water increases, in spite of the remarkable change of K. Recently, Saito[4] and Ishihara[5] calculated theoretically the concentration dependence of specific viscosity, and found that $k=0.4$ as first approximation for spherical particles. This value is close upon the experimental data obtained by the present author.

Summary

Viscosities of the dilute solutions of polyvinyl acetate have been measured in acetone-water mixtures of varying proportions. The experimental results are well expressed by the following equation

$$\eta_{sp}/c = [\eta] + k[\eta]^2 c.$$

The intrinsic viscosity ($[\eta]$) shows a slight maximum at about 5% of water content, and decreases gradually for larger content of water. The value of k is close upon 0.4 and does not vary appreciably.

The author expresses his sincere thanks to Prof. Jitsusaburo Sameshima for his kind guidance and encouragement. The expense of this work has been defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the author's thanks are due.

Chemical Institute, Faculty of Science, the University of Tokyo.

(5) N. Saito, Lecture at the special meeting of the Physical Society of Japan, on May 1, 1949.

(6) A. Ishihara, Lecture at the special meeting of the Physical Society of Japan, on October 23, 1949.

Fluorometric Microdetermination of Uranium. I. Fluorescent Material for the Determination

By Masaki NAKANISHI

(Received December 27, 1949)

Introduction

Hexavalent compounds of uranium, the uranyl salts, have peculiar fluorescent property. Their fluorescence is observed by irradiating either the crystal or the solution with the ultraviolet light. This phenomenon is utilized to detect or determine a small amount of uranium in analytical chemistry, and has found its use in the microdetermination of the element.[1] On the other hand, however, another type of fluorometric method is possible, in which uranium is brought into an activator of some solid solution (so-called fluorescent material), and this method will be treated in this paper.

The activating action of uranium on fluorescent materials in solid solution state was widely studied by E.L. Nichols and M.K. Slattery.[2][3][4] They found that sodium fluoride

(1) C.W. Sill and H.E. Peterson, *Anal. Chem.*, **19**, 646 (1947).

(2) E.L. Nichols and M.K. Slattery, *J. Opt. Soc. Am.*, **12**, 449 (1926).

(3) M.K. Slattery, *J. Opt. Soc. Am.*, **19**, 175 (1929).

(4) M.K. Slattery, *Proc. Nat. Acad. Sci.*, **14**, 777 (1928).

and lithium fluoride, activated by the addition of a small amount of uranium, show bright luminescence of yellow and green hue respectively in the ultraviolet light, the brightness of which exceeds that of solid uranyl salts under the same excitation.

For the detection of a minute quantity of uranium, J. Papish and L.E. Hoag,[5] and then F. Hernegger[6] recommended the fluorescence method, in which the fluorescent material, formed with sodium fluoride as a ground material and uranium as an activator, is used.

Afterwards F. Hernegger and B. Karlik[7] developed this method into the microdetermination of uranium.

In connection with the geochemical researches on radioactive elements, which have been pursued more than ten years in this laboratory, the writer examined the details of this fluorescence method and confirmed it to be available, especially for geochemical purposes, for which the determination of less than one millionth gram of uranium was required.

Even in comparison with the radioactivity measurement method,[8] which has been hitherto most sensitive for radioactive elements, this fluorescence method is more delicate, so far as uranium is concerned, on account of the feeble radioactivity of uranium.

Fluorescent material of sodium fluoride activated by uranium shows a vivid yellow fluorescence, when irradiated with rays of the ultraviolet region. The intensity of the fluorescence varies remarkably according to the uranium content of the fluorescent material, and by the present treatment no more than 10^{-9} gram of uranium is necessary to produce the noticeable fluorescence.

Fluorescent Material of Sodium Fluoride Containing Uranium

Relation between Uranium Content and Fluorescence Intensity.—Some different quantities of uranium were mixed in aqueous solution with about 20 mg. of sodium fluoride. After drying, fluorescent beads were prepared by fusing the residue on a platinum loop, the procedure of which will be detailed in the following papers. Fluorescence of each bead caused by the excitation of ultraviolet rays was investigated regarding its luminescence intensity by the photographic spectrophotometry. Fig. 1 shows the results: the ordinate (intensity) is drawn to an arbitary scale, the abscissa shows the amount of uranium contained in about 20 mg. of sodium fluoride. As is seen in Fig. 1, the maximum intensity is reached at about 5×10^{-5} g. of uranium in a bead. In the photographic experiment concerned, the time of exposure was too short to catch an image corresponding to 10^{-8} g. of uranium. By visual observation, however,

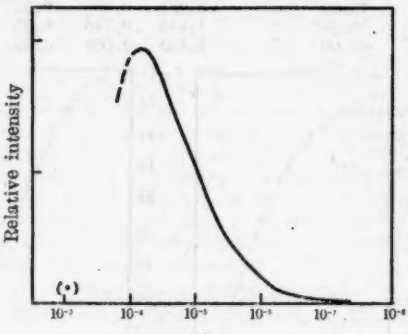

Fig. 1.—Fluorescence intensity.

fluorescence due to 10^{-8} g. of uranium is still bright, and as uranium content decreases from 10^{-8} g., the fluorescence becomes rapidly fainter and finally almost vanishes at about 10^{-9} g. Pure sodium fluoride presents no fluorescent phenomenon.

In case a bead contains 10^{-4} g. of uranium or more, it is supersaturated with regard to uranium, and the excessive uranium compound interferes with the proper formation of fluorescent material, the intensity of which depends much upon the experimental conditions. Therefore the fluorescence intensity of 10^{-3} g. of uranium indicated in Fig. 1 is no more than an example.

If we consider the narrow region of uranium content, the fluorescence intensity is reasonably regarded to be linear to the uranium content between about 10^{-5} and 10^{-9} g. On this base lies the microdetermination method of uranium, and its favorable range of application extends from 10^{-5} to 10^{-8} g. of uranium.

Fluorescence Band Spectrum.—Like many other fluorescent and phosphorescent substances, this fluorescent material has some emission bands. To obtain the quantitative spectral energy distribution of the luminescence, the photographic spectrophotometry[9] was applied here again.

As an intensity scale, the tungsten filament lamp was used. Its brightness was reduced to some different extents, and the corresponding spectra were photographed on a plate, together with the spectrum of the fluorescence in question. The time of exposure was the same for

(5) J. Papish and L.E. Hoag, *Proc. Nat. Acad. Sci.*, **13**, 726, (1927).

(6) F. Hernegger, *Anz. Akad. Wiss. Wien*, **70**, 15, (1933).

(7) F. Hernegger and B. Karlik, *Sitz. Akad. Wiss. Wien, Abt. IIa*, **144**, 217, (1935).

(8) Wm. D. Urry, *Am. J. Sci.*, **239**, 191, (1941).

(9) H.B. Dorgelo, *Phys. Z.*, **26**, 756, (1925).

each spectrum. The work was made at room temperature, and an ordinary panchromatic plate was employed. The bead of sodium fluoride contained 10^{-4} g. of uranium, nearly the optimum proportion to form the fluorescent material. A filtered mercury vapour lamp of high pressure was employed to excite the bead, where the effective ultraviolet light extended from 2480 to 3660 Å. Then followed the determianation of blackness of the photographic image corresponding to these spectra with the microphotometer, and next the calculation of spectral energy distribution relative to the standard lamp, and at last correction for inequality of the standard lamp through the spectral region. Spectral energy distribution of the fluorescence thus obtained is graphically shown in Fig. 2. The fluorescence bands cover the region from 5300 to 6150 Å of wave length. It is obviously seen in Fig. 2 that the

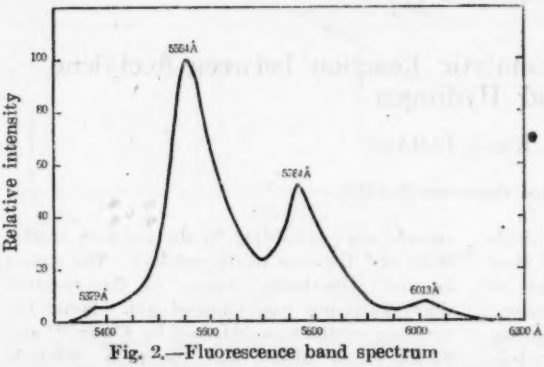

Fig. 2.—Fluorescence band spectrum

fluorescence includes four distinct partial bands, in which two are remarkably strong. Relative intensity of these four band maxima are tabulated.[10]

Wave length in Å	Relative intensity
5379	5.8
5554	100
5764	51.8
6013	7.6

Hygroscopic Tendency.—The prepared fluorescent material is slightly hygroscopic. The disc-like bead of this material on a platinum loop is often dewed with water from atmospheric moisture in wet weather. The fluorescence intensity of the bedewed bead becomes less intense especially for the smaller uranium content. Even after drying and refusion, it does not reveal its proper intensity. In most cases this treatment makes the fluorescence more intense, because it means prolonging the time of fusion, or in other words increased loss of ground material, sodium fluoride, by evaporation. Therefore the fluorescent beads of both sample and standard must be prepared immediately before the comparison in the same way. And if it is required to reserve the beads, they should be kept in a desiccator.

Interfering Substances.—We can enumerate many examples of the fluorescent material which is remarkably affected by a small amount of impurities; but the fluorescent material applied to the uranium determination is fortunately less affected by other impurities.

The interferences by other impurities will be generally examined on the analytical-chemical side.

Niobium and zinc are reckoned to be the only elements, except uranium, which act as activator for sodium fluoride. They produce luminescence of clearer green and orange hue respectively and less intense. But it is usually unnecessary to pay particular attention to niobium, because it is only a very minor contamination of ordinary samples, but special mineralogical or metallurgical ones, and furthermore is easily separated from uranium by the chemical procedures. Almost the same applies to zinc. Although we can not neglect the influence of zinc, inasmuch as it is a relatively abundant element, it is eliminated by any proper chemical treatment.

Impurities which form luminescent substances with uranium are to be removed too. These impurities include fluorides of other alkali metals and calcium, strontium chloride, borax, microcosmic salt, sodium phosphate, etc.[3] Generally their fluorescence is not so bright as that of sodium fluoride. It depends also upon the purification of sodium fluoride and careful manipulation to prevent this kind of interference.

Next in order is reference to the interferences of heavy metals. For example, iron is most likely to contaminate and severely reduces the intensity of fluorescence by the probable absorption of ultraviolet light. Manganese colors the bead green, but has almost no influence on the flourescence. Thorium, if more than 10^{-5} g. of the element is mixed in the bead of about 20 mg. weight containing 10^{-8} g. of uranium, gives a somewhat orange color to the bead, but reduces only a little the fluorescence intensity. Generally speaking, heavy metals can hardly disturb the test, if they are removed by any means to an imponderable trace comparable with the present amount of uranium.

Some earths, e.g. silica, titania, form complex fluorides with sodium fluoride which do not take the place of sodium fluoride in the

(10) As for the wave length of band maxima, Nichols and Slattery (ibid.) reported at 534, 557, 577, 606, 634 mμ, and Hernegger and Karlik (ibid.) at 555, 577, 602, 626 mμ. For the fine structure at the liquid air temperature, see (3).

luminescence test, but their influence can be prevented, too, by treating with more sodium fluoride.

Then insoluble matters, *e.g.* alumina, often cover the effective surface of the bead, if they remain much in the bead after fusion, which diminish or extinguish the luminescence to a greater extent. These difficulties are avoided in practical cases by ordinary chemical treatments, the details of which will be mentioned in the succeeding papers. After all, it is concluded that every kind of contamination is undesirable, but it interferes little if its quantity is as small as that of the uranium.

Summary

As the most sensitive method for the determination of uranium, the fluorescence method is recommended. Fluorescent material of sodium fluoride containing a small amount of uranium (10^{-4} to 10^{-9} g. per 20 mg. of sodium fluoride) was investigated in this paper from several sides.

Relation between fluorescence intensity and uranium content is described, and the fluorescence band spectrum was studied by spectrophotometry, regarding its spectral energy distribution.

Various interfering factors to this method were examined too, especially as to its analytical application.

In conclusion, the writer wishes to express his hearty thanks to Prof. K. Kimura, to whom he is much indebted for the continual stimulation and the kind guidances.

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Selective Catalysis. The Catalytic Reaction between Acetylene and Hydrogen

By Kenzi TAMARU

(Received December 28, 1949)

Many investigations have already been made on the hydrogenation of acetylene.[1]-[12] Most of them, however, deal with the products of hydrogenation by the flow method, no attention being paid on the kinetics of reaction. Generally speaking, when acetylene and hydrogen react on a hydrogenation catalyst, there occur three kinds of reactions simultaneously, that is

1) $C_2H_2+H_2=C_2H_4$
2) $C_2H_4+H_2=C_2H_6$
3) $nC_2H_2+mH_2=C_{2n}H_{2(n+m)}$

These reactions are considered as proceeding at various rates according to the reaction conditions and the state of the catalyst. The reason for the remarkable change of the reaction velocities is not well clarified yet. Some interesting results were obtained by Kwan[11] and Farkas[8] on nickel and platinum catalysts repectively. The plausible explanations, however, on the selective action of the catalysts have not been obtained. In the present report some results of the experiments are described on the kinetics of the reactions between acetylene and hydrogen using palladium alumina as catalyst.

Experimental Procedure

The acetylene gas was generated from calcium carbide and water, and purified by the usual method.* Hydrogen was obtained by the electrolysis of water. Palladium alumina catalyst (1 : 100) was prepared by Sano's method[13] from palladium chloride solution. The alumina used was the sample made for the purpose of chromatography by Nippon Aluminium Co.

The experiments were undertaken by the usual static method, the volume of the reaction vessel being about 120 cc. The reacting gas was taken out by a Toepler pump and analysed. The analysis of acetylene and ethylene was carried out according to the method of Treadwell[14] modified by Fujio.[15] Acetylene, ethylene and heavy

(1) Paal and Hohengger, *Ber.*, **48**, 275 (1915).
(2) Ross, Culbertson and Parsons, *J. Ind. Eng. Chem.*, **13**, 775 (1921).
(3) Morris and Reyerson, *J. Phys. Chem.*, **31**, 1332 (1927).
(4) Johnson, Brit. Pat., 294, 787 (1927).
(5) Yoshikawa, *Bull. Chem. Soc., Japan*, **7**, 201 (1932).
(6) Ackermann, *Brennstoff-Chem.*, **18**, 357 (1937).
(7) Fischer and Knorr, *Z. Elektrochem.*, **43**, 608 (1937).
(8) A. Farkas and L. Farkas, J. *Am. Chem. Soc.*, **61**, 3396 (1939).
(9) Cremer, Knorr and Plieniger, *Z. Elektrochem.*, **47**, 737 (1941).
(10) Sheridan, *J. Chem. Soc.*, **1944**, 378; *ibid.*, **1945**, 133, 301, 305, 470.
(11) Kwan, *J. Phys. Chem. Res. Inst., Tokyo*, **23**, 205 (1944).
(12) Yamanaka, *J. Phys. Chem. Res. Inst., Tokyo*, **25**, 329, 481 (1949).

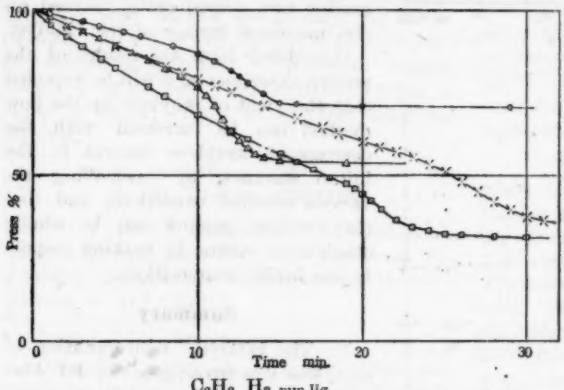
* Refer Vanino's "Präparativen Chemie"

(13) Sano, *J. Chem. Soc., Japan*, **58**, 393 (1937).
(14) Treadwell, *Helv. Chim. Acta*, **2**, 601 (1919).
(15) Fujio and Shirai, *Experimental Reports of Japanese Naval Institute of Fuel*, **4**, No. 4, 47.

hydrocarbons were determined by absorption with the solution of mercuric cyanide, mercuric nitrate and fuming sulfuric acid respectively. After the removal of the above gases, hydrogen and saturated hydrocarbons were estimated by the explosion method using oxygen gas.

Experimental Results

The results of experiments at 30° are shown in Fig. 1, the abscissa of which being pressure and the ordinate time. In the course of reaction it was observed that the rate of hydrogenation increased rapidly at a certain stage. An example of the change of composition with time is shown in Fig. 2. In this figure the



	C_2H_2	H_2 mm.Hg	
Fig. 1—⊙—	78	404	(0.044g catalyst)
—△—	120	350	(0.082g 〃)
—×—	200	258	(0.147g 〃)
—◆—	235	250	(0.261g 〃)

solid line shows the total gas pressure, and the dotted lines show the partial pressures of the component gases. It can be seen, from Fig. 2, that the hydrogenation of acetylene proceeds in two distinct stages. At first all acetylene is hydrogenated or polymerized, and after that ethylene is hydrogenated to ethane. The start of the second stage is indicated by a sudden increase in the rate of hydrogenation. The sudden drop of the gas pressure corresponds to the moment when all acetylene has been used up.

The initial velocity of hydrogenation is proportional to the amount of the catalyst used. The dependence of the reaction products on the initial composition is shown in Fig. 3, the ordinate of which shows the final pressure relative to the initial one, and the abscissa the initial content of acetylene. The initial pressures of gas range from 450 to 500 mm. Hg. The solid line shows the dependence of the total gas pressure of the reaction product on the initial composition, and the dotted lines the final content of hydrogen, ethylene, ethane or acetylene. The broken line indicates the ratio of final non-polymerized acetylene to the initial one, taking in the ordinate the ratio in percentage of acetylene. The chain line expresses the values of the velocity constant calculated from each experiment. The way of calculation of the velocity constant will be given later. Fig. 3 shows that if the initial content of acetylene is approximately 41% or 51%, the reaction products are wholly ethane or ethylene respectively, and that the polymerized portion of, acetylene increases with the initial content of acetylene.

The hydrogenation of ethylene which occurred in the last half of the reaction, is faster than the formation of ethylene at 30°, but as the reaction temperature is raised, the difference in the rates of the two reactions grows smaller till the former in turn becomes slower than the latter. An example of the experiment at 74° is shown in Fig. 4. It is to be noticed that at higher temperature the formation of ethane proceeds appreciably while acetylene is being hydrogenated.

From these results the energy of activation for the hydrogenation of acetylene is calculated to be 12 kilocalories. This figure is somewhat higher than the energy of activation for the hydrogenation of ethylene, which has been determined to be 9 kilocalories in the same catalyst and at the same temperature range.

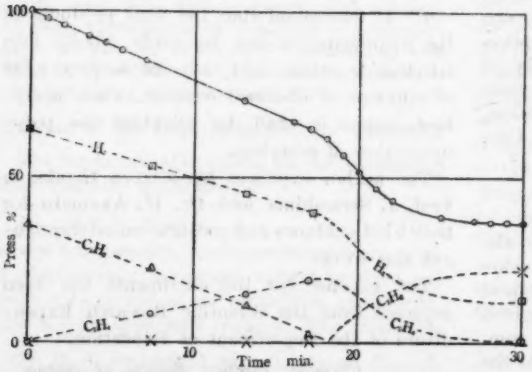


Fig. 2.—C_2H_2 182mm.Hg. + H_2 332mm.Hg. Pd-Alumina catalyst 0.105 g. at 30°.

Discussion

The feature of the hydrogenation of acetylene on palladium alumina catalyst at room temperature is that the hydrogenation takes place in two distinct steps. At the first step the acetylene is converted into the ethylene and th

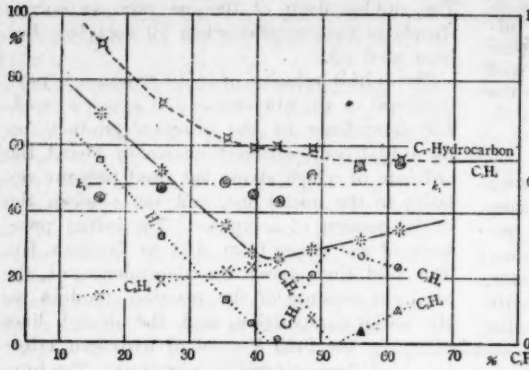


Fig. 3.

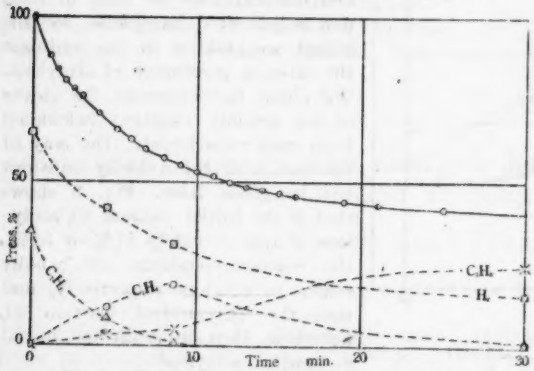


Fig 4.—C_2H_2 $182_{mm.Hg}$ + H_2 $331_{mm.Hg}$ Pd-Alumina 0.025 g.

polymers, and at the second step the ethylene is hydrogenated to ethane. The second reaction proceeds after all acetylene has been used up.

The author considers that the selective hydrogenation may be due to the difference of the adsorbability of acetylene and ethylene on the catalyst, and not to the difference of the velocity of the hydrogenation reaction. The dependence of the rate of hydrogenation on the pressure of acetylene and hydrogen can readily be explained by the strong adsorption of acetylene on the catalyst. The velocity of the first stage of hydrogenation of acetylene may be expressed by the following equation, which is analogous to the one given by Cremer,[9]

$$-\frac{dP}{dt}=\frac{k_1 P_{H_2}}{1+b P_{C_2H_2}},$$

where P denotes the pressure of gas, t the time and, b and k_1 the constants. The velocity constant k_1 calculated from the initial velocities by using the value $b=0.0031$ is given in Fig. 3, the pressure being expressed in mm. Hg and the time in minutes. However, as the polymers produced in the first stage cover the surface of the catalyst, some corrections must be applied for the retarding action in the calculation. The second stage of the reaction, the hydrogenation of ethylene, can be treated approximately as a first-order reaction.

At high reaction temperature, the first stage becomes faster than the second one, the activation energy of the former being greater than that of the latter. In this case the ethane formation is observed during the first stage. This suggests the fact that the adsorption of acetylene decreases at the raised temperature and the ethane formation can, consequently, proceed on the uncovered surface of the catalyst.

Considered from the results of the present experiments, it will be expected that the yield of ethylene by the flow method can be increased with the decrease of acetylene content in the initial reactant, by controlling the various reaction conditions, and that the reaction product can be wholly ethylene or ethane by making properly the initial composition.

Summary

1) The catalytic hydrogenation of acetylene was investigated by Pd-Alumina under various conditions.

2) The hydrogenation of acetylene proceeds in two distinct steps. The first step consists of the reduction and polymerization of acetylene, and the second step the reduction of ethylene to ethane. The second reaction starts after all of the acetylene is reduced to ethylene, and is indicated by a sudden increase in the rate of hydrogenation.

3) The results indicate that acetylene is strongly adsorbed on the surface of the catalyst and the inhibition of the hydrogenation by acetylene is pronounced.

4) It was found that the final products of the hydrogenation can be made wholly into ethylene or ethane and that the highest yield of ethylene is obtained possibly, when acetylene content is small, by avoiding the polymerization of acetylene.

The author expresses his sincere thanks to Prof. J. Sameshima and Dr. H. Akamatu for their kind guidance and encouragement throughout this work.

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On the Viscosity of the Uranium Hexafluoride

By Kunihiko KIGOSHI

(Received December 28, 1949)

The viscosity and Sutherland's constant of the uranium hexafluoride were measured with the Maxwell type viscosimeter. The sample of the uranium hexafluoride was obtained by the reaction of fluorine gas on the uranium carbide, and the fluoride obtained was purified by the sublimations under the room temperature repeated several times. The first two sublimation processes were carried out through the dehydration tube which was charged with resublimed phosphorus pentoxide. The purified sample became colorless and clear crystals having a vapor pressure expressed by the following formula,

$$\log P_{UF_6}(\text{mm.Hg}) = 10.023 - 2486/T + 0.0012\,T, \qquad (1)$$

where T is absolute temperature. The measurements of vapor pressure were performed by a statical method at the temperature interval between 0° and 34.6°.

Apparatus

An oscillating-disk viscosimeter[1] with gold plated copper disks was used. An oscillating disk having a diameter of 30 mm. and thickness of 2 mm. was placed between two fixed disks. The distance between inner surfaces of the two fixed disks was 3 mm. The oscillating disk was adjusted to a place at the middle of these disks, and the distances which separate the oscillating disk and upper and lower fixed disks were kept equal 1.0 mm. The oscillating disk was suspended by platinum wire, of which the length about 20 cm. and diameter 0.05 mm. A thick copper wire of about 5 cm. length was used for the connection of the platinum wire and the oscillating disk. At the top of this copper wire a small mirror was cemmented. These metal works were contained in the quartz glass tube with a quartz glass window. All these apparatus were immersed in a thermostat. Amplitudes of succsesive oscillations were observed by means of a telescope with cross hair, with the aid of an illuminated scale.

Method of the Determination of Viscosity

The fundamental equation for the oscillating-disk viscosity apparatus is

$$\eta = (\lambda - \kappa)/Kt, \qquad (2)$$

where η = viscosity, λ = logarithmic decrement, κ = logarithmic decrement caused by wire and mirror, t = period of one oscillation, in seconds, and K = the apparatus costant. The correction for end effect and slipping coefficient at the metal surfaces can be neglected in this case.[2] We can obtain the logarithmic decrement λ with the following formula,

$$\ln(a_\nu - b_\nu) - \ln(a_{\nu+n} - b_{\nu+n}) = n\lambda\varphi \qquad (3),$$

where a_ν and b_ν are the successive observations of the amplitudes of left and right sides of an oscillation. Suffixes of ν and $n+\nu$ mean the observations about the ν- and $n+\nu$-th oscillations respectively. The period of one oscillation t (=16.03 sec. in this apparatus) was constant throughout the observations, then the equation (2) may be written as follows,

$$\eta = H(\lambda - \kappa), \qquad (3)'$$

where H is an apparatus constant. The constant κ and H were obtained from the following observations.

A main part of the logarithmic decrement κ is derived from the energy losses in platinum wire. The friction of mirror has a small contribution on κ[2] therefore we may neglect it and take κ as a wire constant. To obtain the wire constant the logarithmic decrement was measured under the high vacuum. A series of six observations of a_ν, and b_ν with $n=30$ were performed in each determination. The average of κ was 0.000728 and each value agreed to within 1 per cent. The apparatus constant H was determined by logarithmic decrement with air at temperature 15.2°. The averaged value was $\lambda = 0.010667$. When we take the viscosity of air as $\eta = 179.62\,\mu$ poises,[3] the constant H may be derived as $H = \eta/(\lambda - \kappa) = 18073 \times 10^{-6}$.

To check the apparatus, the viscosity of hydrogen was measured at temperature 12.9°. The observed value was $\eta = 86.7\,\mu$ poises, which agreed well with published values.[3] There was no great change in apparatus constant with temperature variation, since the measurements with air at temperature 40.5° and 15.2° gave probable value of Sutherland's constants for air. The observed values of λ was 0.011321 at temperature 40.5°, and Sutherland's constant $S = 104$ was obtained from these values. Hydrogen used in this experiment was obtained by electrolysis and purified through heated tube filled with platinized asbestos and a trap cooled with liquid oxygen. Dry air was purified through concentrated sodium hydroxide solution and a trap cooled with liquid oxygen.

(1) B. P. Sutherland and O. Maass, *Can. J. Research*, **6**, 428 (1932); E. Kanda, *J. Chem. Soc. Japan*, **58**, 804 (1937).

(2) G. E. MacWood, *Physica*, **V**, No. 5, 374, 763 (1938).

(3) H. L. Lohnston and K. E. McCloskey, *J. Phys. Chem.*, **44**, 1053 (1940).

The observations using these gases were performed under an atmospheric pressure.

Viscosity of the Uranium Hexafluoride

Preliminarily, highly evacuated apparatus was filled with uranium hexafluoride by sublimation from the container of UF_6 crystals. The viscosities were measured at approximate 10° intervals from 14.5° to 44.7°. The observed values of λ and η are shown in Table 1. The sample for the observations at the temperature 14.5° was filled by the sublimation under 8°. For the observations at the temperature higher than 20°, the sample was sublimed at 18°. Therefore in each case the pressure of uranium hexafluoride in apparatus was 33 mm.Hg and 68 mm.Hg respectively. The measurements of logarithmic decrements taking the series of

Table 1

t°C.	λ	μ poises (obs.)	μ poises (calc.)
14.5	0.00973	162.7×10^{-6}	162.4×10^{-6}
26.3	0.01013	169.9 〃	170.1 〃
35.2	0.01045	175.7 〃	176.0 〃
44.7	0.01083	182.5 〃	182.2 〃

eleven observations of a_ν and b_ν with $n=5$ (*e. g.* $\nu=10, 15, 20\ldots\ldots70$) agreed to within 0.2 per cent.

The Sutherland's formula,

$$\eta=CT^{3/2}/(T+S) \qquad (4)$$

can be fitted to the observed values using the following numerical constants:

$$C=28.44\times10^{-6}, \qquad S=566.8$$

The calculated values from these expression are shown in Table 1.

By the use of the following formula,

$$C=\frac{5}{16\,\sigma^2}\left(\frac{km}{\pi}\right)^{\frac{1}{2}}, \qquad (5)$$

where k=Boltzmann constant, σ=molecular diameter, m=mass of the molecule, we can obtain the molecular diameter of uranium hexafluoride.

$$\sigma=4.20\ \text{Å}.$$

When we assume that the observed viscosities are proportional to T^s, then $s=1.16$ in this case. The rigidity ν of the molecule given by $s=1/2+2/(\nu-1)$ is obtained for uranium hexafluoride as $\nu=4.03$.

Summary

On the uranium hexafluoride obtained by the reaction between fluorine and uranium carbide, the viscosity was measured between 14.5° and 44.7°. The purification of uranium hexafluoride was performed by several repeated sublimation. The oscillating-disk viscosimeter was used in this experiments and its apparatus constant was obtained by the observation of the apparatus filled with air. The molecular diameter of uranium hexafluoride was determined from the Sutherland's constant, and the rigidity of the molecule was also obtained from the observed values.

The studies on uranium hexafluoride have been performed during February, 1945 at Dr. Nishina's Laboratory of the Institute of Phisical and Chemical Research in Tokyo. The author wishes to express his hearty thanks to Dr. Nishina for his valuable advice.

Geochemical Laboratory,
Meteorological Research Institute,
Tokyo

J. Sameshima.

Professor Jitsusaburo Sameshima

Professor Jitsusaburo Sameshima who celebrates his sixtieth birthday this year, on July 3rd, was born in 1890 in the city of Osaka. He graduated from the Chemistry Department of Tokyo Imperial University in 1914. In this university he devoted himself to the research work on physical chemistry under the guidance of Professor Kikunae Ikeda. In the spring of 1918, during the 1st World War, he was sent abroad as a research scholar of the government. He worked in the laboratory of Professor T. W. Richards at Harvard University, U. S. A., where he was influenced by the great master of exact chemical experiments. While he was in Europe he studied under Professor F. G. Donnan in London, Professor J. Perrin in Paris and Professor H. K. Onnes in Leiden.

On his return home in 1921, he was appointed to an assistant professor and in the following year to a professor of Tohoku Imperial University in Sendai. In March 1923, he became Professor of Physical Chemistry in Tokyo Imperial University. Since then he has held this position continuously for twenty seven years. From 1939 to March 1950 he was Director of the Chemical Institute of Faculty of Science, the University of Tokyo.

Professor Sameshima's work on physical chemistry is chiefly connected with the theory of solution, properties of gas, sorption of gas by solid, and surface and colloid chemistry. The papers on the vapor pressure of binary solutions were published in 1918 in the Journal of American Chemical Society. These papers are often referred in the college text-books of physical chemistry. The separation of gas mixtures by atmolysis, i.e., the diffusion through porous plate, drew his attention and an equation was derived on the efficiency of separation in 1923. Needless to say that this phenomenon has an important meaning in the isotopic separation. He, then, carried out a series of measurements on the sorption of gases on solid matters. He proposed the opinion that the taking of gases by charcoal is the phenomenon of sorption in the interstices of carbon atoms and he obtained the equations of the velocity of sorption. He studied the sorption of gases by zeolite and other minerals. His work on surface and colloid chemistry includes the problems on viscosity, protecting colloid, surface pressure, foam etc. He devised a simple method of measuring the friction coefficient and obtained some interesting results on the surface chemistry. He published several books on chemistry, among which the "Experimental Method of Physical Chemistry" is most widely known in Japan.

His connection with the Chemical Society of Japan is worth mentioning. He is the actual founder of this "Bulletin." The Chemical Society of Japan had only one publication printed in the Japanease language when he became the professor of Tokyo Imperial University. In Japan there was no regularly issued publication on chemistry printed in any European languages. Professor Sameshima eagerly insisted on the utmost necessity of internationalizing Japanese chemical publication. Thus, by his effort, the "Bulletin of the Chemical Society of Japan" started as a monthly journal in January 1926. All the editorial and distribution business were done almost by himself alone. More than four hundred copies were distributed throughout the world mostly without charge. This was certainly a big service and contribution of the Chemical Society of Japan to the learning circles of the world. His editorship continued from 1926 to 1930. In 1935 he was elected President of the Society.

Professor Sameshima, enjoying his excellent health, is devoting his full time to the advancement of chemistry in Japan.

July 1950

The Editor

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